OPTICAL ROTATORY POWER OF ORGANIC ACIDS AND THEIR DERIVATIVES IN AQUEOUS AND NON-AQUEOUS SOLUTIONS.

by

Margaret F. Ritchie, B.Sc.

Thesis for the Degree of Ph.D.

October 1934.

CONTENTS.

INTRODUCTION.

It has long been recognised that the rotation of a substance in solution is controlled by various factors, such as the structure of the optically active substance, the nature of the solvent, the concentration and temperature of the solution, and the wavelength of the light employed. The importance of the first-named has been stressed since the beginning of the study of optical activity. Thus Biot, examining the fundamental difference between the rotation of inorganic substances such as quartz, and that of the organic substances then studied, namely oil of turpentine, cane sugar, and tartaric acid, emphasized that the inorganic substances exhibit optical activity in the crystalline form only, whilst organic substances are active in the solid, liquid and gaseous states; he concluded, therefore, that in the former case the activity is determined by the arrangement of the crystalline units, while in the latter case the determining factor is the constitution of the ultimate "particles". His ideas may now be expressed by saying that the activity of a quartz crystal depends on the arrangement of the molecules in that crystal, while that of sugar depends on the structure of the molecule itself.

In 1848, Pasteur, after completing his study of the crystalline form of the tartrates, suggested that the/

the cause of optical activity lay in some asymmetry of the molecular structure. His work was carried out before Kekulé's theory of molecular structure, or even Frankland's theory of valency had been put forward, so that it was not possible at that time to give a model of the asymmetric tartaric acid molecule. The discovery of such molecular asymmetry, however, was the foundation of the theory of spatial arrangement of atoms, propounded later by van't Hoff and Le Bel. It was pointed out by van't Hoff that all the optically active compounds then known, contained at least one carbon atom attached to four different atoms or radicals. Thus we have the all-important conception of the tetrahedral asymmetric carbon atom. It should be noted that van't Hoff, like Pasteur, did not refer optical activity to the presence of an asymmetric carbon atom alone, but rather to the dissymmetry, which such an atom introduced into the molecule. The truth of such a generalisation is, of course, now fully realised, since numerous compounds have been prepared which, containing no asymmetric carbon atom, are yet asymmetric as a whole, and optically active.

It is evident, however, that the simplest approach to the examination of an asymmetric molecular system is by consideration of an asymmetric carbon atom, and it would appear that the rotation must depend on the difference of some collective property of/

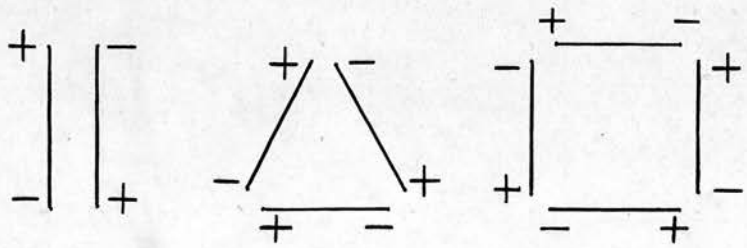
of the four groups. Any disturbance of the groups by various factors must produce a corresponding change in the rotation. It was to the elucidation of such factors that research naturally turned. Guye assumed that the rotation depends essentially on the masses of the four groups and the distances of their centres of gravity from the centre of the tetrahedron. This theory agreed with the experimental results in some series, but Guye himself and others showed that the presence of two different groups with equal masses did not destroy activity as the theory demands. Crum Brown in 1890 suggested that to each of the four groups a factor K , representing the composition and constitution should be ascribed, the combination of such K functions, expressed as a continued difference product, giving an expression for the rotatory power. It is important to note that Crum Brown showed, that if K_1 of one group could be gradually changed from a value less than to a value greater than K_2 of another group, then the rotation passed through zero ($K_1 = K_2$), and then changed in sign. No method of estimating such functions, however, was suggested.

The electro-magnetic nature of light having been recognised, it is natural to assume that any electrical property of the asymmetric molecule might conceivably be a factor of importance in determining the ultimate rotation/

rotation. Thus, within the last few years, the problem has been attacked from the polar standpoint. A polar molecule is one in which the mean electric centres of positive and negative charges do not coincide i.e. an electrical dipole is present. The effect of such a dipole is measured by its electrical moment, which is defined as the product of the distance between the electrical centres of positive and negative charges and the charge on one of them, and can be calculated from data referring to the dielectric constant and refractivity of the compound. The determination of dipole moments by C.P. Smyth, J.W. Williams, K. Höjendahl, J. Errera, and others, led to the conclusion that the dipole moment is practically independent of the hydrocarbon radical to which the substituent is attached, that is, it is a characteristic of the substituent group alone. In 1924 Rule (J.C.S., 1924, 1121) advanced the hypothesis that the rotatory power of a molecule is a function of the dipole moments of the four groups attached to the asymmetric atom, and that the influence of a substituent on the rotation would depend upon its polarity. The results of a large number of investigations have established a definite correlation between the polarity of the substituent group and the rotatory power of the molecule.

As a result of the experiments of Rule and Mitchell/

Mitchell (J.C.S., 1926, 3202) it was suggested (Rule J.C.S., 1927, 58) that polar groups present in the solvent would also exert an influence on the optically active solute, leading to changes in rotatory power. In a detailed investigation of solvent effect, undertaken by Rule and McLean (J.C.S., 1931, 674), the compound chosen was l-menthyl methyl naphthalate, in virtue of the sensitiveness of the optical rotation to change of solvent. The solvents selected fell into four main types - namely, simple derivatives of the four hydrocarbons, methane, ethane, benzene and naphthalene. It was found that in each series, the rotatory power of the solution decreased as the dipole moment of the solvent increased. It was concluded that the observed effects were due to the influence of the solvent dipole upon the internal electric field of the solute, acting either through deformation or dipole association i.e., a linking up of the dipoles to form closed chains, so as to minimize the external electric field (cf. diagram)



It is thus to be expected that the dipoles in the solvent molecules will be attracted to the dipoles of the solute; the stronger the solvent dipole, the greater will be the tendency to associate, with a corresponding reduction in the internal molecular field exerted by each dipole group. In an optically active molecule the contribution of a given substituent or dipole group to the total activity may be such as to raise or lower the actual rotation, and hence association through this particular substituent merely diminishes its characteristic contribution to the total activity, leading to a lowering or raising of the magnitude. In the majority of cases, a highly polar substituent situated near an asymmetric atom makes a positive contribution to the optical rotation; an increase in the degree of association may thus be expected to lower the rotatory power. It should then be possible to trace the same effects in the concentration curves of such an optically active compound in a non-polar solvent. In concentrated solutions the molecules of the solute will associate with each other leading in the majority of cases, to a lower rotation. As the dilution increases the associated molecules will be progressively split up, and an increased rotation will result. Thus it is found experimentally (Rule and Smith, J.C.S., 1933, 376) that, while association of the solute molecules either with themselves or with the molecules of a polar solvent,/

solvent, does not always lead to a decrease in rotation, increase of the degree of association in a non-polar solvent (i.e. an increase in concentration) always leads to a change in the same sense as that brought about by association with the molecules of a polar solvent.

As Rule and McLean point out, the actual strength of the dipole in the solvent need not be the only factor affecting the mechanism of solvent action. From a consideration of the following table, it will be seen that, as the hydrocarbon residue attached to the iodine atom increases in size, the rotation of methyl menthyl naphthalate dissolved in the iodo-compound rises, i.e. the direction of change is towards that found with a non-polar solvent (Rule and McLean loc. cit.)

Solvent	$[M]_{5461}^{20}$
CH_3I	- 336°
C_2H_5I	- 383°
C_6H_5I	- 465°
S - $C_6H_3(CH_3)_3$	- 583°

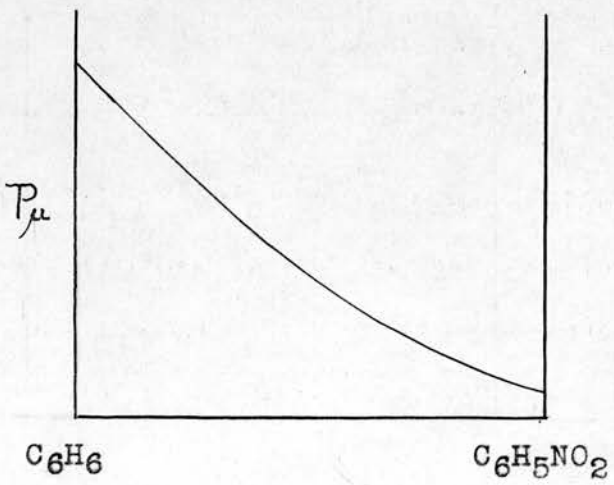
Such an effect is attributed to two factors. Firstly, the polar substituent present in the larger molecule will come into contact less frequently with the polar group in the optically active molecule, and secondly, the screening of the dipole in the solvent by the bulky/

bulky hydrocarbon residue will hinder association.

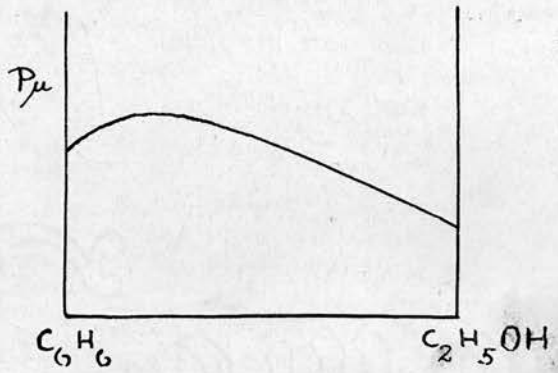
Another factor which must be taken into account in an attempt to explain solvent action, is the association of solvent molecules with themselves. This may take place in some such ways as the following:-

(1) $\overset{-}{\underset{+}{\rule{2em}{0.4pt}}}\ \overset{-}{\underset{+}{\rule{2em}{0.4pt}}}$ (2) $\overset{-}{\underset{+}{\rule{2em}{0.4pt}}}\ \overset{+}{\underset{-}{\rule{2em}{0.4pt}}}$

In the first case, the dipole moment would be larger than that of a single molecule, while in the second case the dipole moment would be zero. When the associated solvent is diluted with a non-polar medium such as benzene, the tendency will be for the complexes to be progressively split up. This is seen from the polarisation curves of binary mixtures of polar and non-polar liquids given by Debye ("Polare Molekeln", Leipzig, 1929). In the case of nitrobenzene and benzene the following curve is obtained:-



This is explained by assuming that the nitrobenzene molecules are associated so as to neutralize each other as in Type (2) above. On the addition of the non-polar constituent, this association is broken up, leading to a rise in the polarisation. In the case of ethyl alcohol and benzene, however, a maximum was obtained in the polarisation curve.



In order to explain this it is assumed that at low concentrations of alcohol association of type (1) predominates. Initial increase in concentration, therefore, produces a rise in the polarisation. When, however, the concentration reaches a certain value, association of type (2) predominates so that the curve falls as in the case of nitrobenzene and benzene.
It would be expected that the above changes in polarisation would be accompanied by corresponding changes in the rotation of an optically active compound in these binary mixtures. This is confirmed by the work of Rule and McLean (loc. cit.) on the rotation of l-menthyl methyl naphthalate in the mixtures nitrobenzene-benzene, and ethyl alcohol-benzene. After correcting/

correcting for the presence of the non-polar diluent, it was found that the rotation curves corresponded satisfactorily to the polarisation curves of the solvent mixtures, an increase in polarisation corresponding to a decrease in rotation and vice versa.

It is thus evident that dipole moments whether present in the solute or in the solvent, have a direct effect on the rotation. Certain abnormalities have however been observed, and these indicate that polarity under certain circumstances may be the chief effect, but is not necessarily the only one.

The case of a salt in solution may in some circumstances be regarded as a limitation of a dipole in which the positive part is more or less removed from the influence of the negative part. As one might expect, the addition of inorganic ions to solutions of certain optically active compounds produces changes in the rotation.

It is convenient in the first place to examine the effect of different inorganic salts with a common anion on optically active substances which are non-ionised. Complications due to the ionisation of the optically active substance, are thereby avoided. Patterson and Anderson (J.C.S., 1912, 101, 1833) investigated/

investigated the influence of inorganic salts, monovalent and divalent, on the rotation of aqueous solutions of ethyl tartrate: it was found that such additions produced a decrease in rotation, the original d-value being displaced in the l-direction. The main influence is assumed to be that exerted by the positive ions, though it is reasonable to expect that the negative ion of the added salt will have a corresponding effect, probably in the opposite sense. The depressing effect of the positive ions may then be arranged in the following order:-

$$Ba^{++} \gg K^{+} > Na^{+} > NH_4^{+} .$$

The divalent Barium ion has a specially great influence, and it is concluded that the effect is related to the valency of the ion. Similar though smaller effects were recorded on the addition of salts to the homogeneous ester. It thus seems improbable that ionisation of the ethyl tartrate plays an important part: it is conceivable that the effect is due to the influence of the positive ion on the polar hydroxyl groups, with a consequent alteration in the general asymmetry of the molecule, and therefore one would expect similar series effects in other suitable non-ionised compounds.

The case of non-dissociated mandelic acid was investigated by Levene and Rothen (J.P.C., 1930, 34, 2567/

2567). The results are given in the following table:-

Salt added	n	$[M]_D^{25^\circ}$
LiCl	0.09	+ 238.1°
NaCl	"	+ 237.6°
KCl	0.4	+ 238.7°
$CaCl_2$	"	+ 253.5°
$SrCl_2$	"	+ 252.2°
$BaCl_2$	"	+ 252.0°
-	-	+ 237.3°

n is the concentration of salt in mols. per litre. The concentration of mandelic acid was in all cases approximately 0.05 M . The absolute values for added halides are higher than that observed for the pure acid solution, and the relative elevating effects of the various salts, considered in relation to their cations, are given by

$$Ca^{++}, \quad Sr^{++}, \quad Ba^{++} \gg K^{+},$$

a series comparable with that cited above.

These results have been regarded as due to the effect of the added ion on the hydroxyl group attached to the asymmetric carbon atom of the optically active substance. Replacement of the hydroxyl group by -O Me or -OM (where M is Beryllium or the Uranyl radical) or by Cl , in compounds such as malic acid, renders the effects to be observed very small. Removal of the hydroxyl group from the asymmetric carbon atom to a/

a neighbouring atom has a similar effect. Campbell (J.P.C., 1931, 35, 1143) found only very small effects on the addition of salts in the case of ammonium α - bromocamphor - Π' - sulphonate, an electrolyte containing no hydroxyl group.

The production of a negative charge by ionisation of the optically active compound must introduce additional complications. Where the substance is a weak acid, the extent to which the order of salt effect (above) is altered will be expected to depend in some degree on the extent of ionisation. Thus Stubbs (J.C.S., 1911, 99, 2265,) found that in the case of l-malic acid in 1.5 molar solution, where the extent of ionisation is undoubtedly small, the rotation was lowered by the addition of inorganic salts, the relative effects of the following chlorides being expressed by the series:-

$$Cs^{+} > Rb^{+} > K^{+} > Na^{+} > NH_4^{+} > Li^{+} > H$$

$$Ba^{++} > Ca^{++} > Mg^{++} > Cd^{++} > Al^{+++} > Zn^{++} > Hg^{++}.$$

Again

$$Ba^{++} > Ca^{++} \gg K^{+} > Na^{+} > NH_4^{+},$$ similar to that found for the unionised ethyl tartrate by Patterson and Anderson (loc. cit.). Taking the negative ions as raising the rotation the series is

$$NO_3^{-} > Cl^{-} > Br^{-} > I^{-}.$$

A similar series of positive ion effects is recorded by/

by Rule and Cunningham (Thesis, Edin. Univ. 1933) for methylene tartaric acid, as well as for the unionised dimethyl methylene tartrate and dimethylene tartrate.

The introduction of the negative charge either by increasing the dilution of the acid solution or by employing solutions of salts of the optically active acid where the degree of dissociation approximates to unity, might be expected to involve changes in the order of the above series by virtue of the attraction or repulsion of the positive or negative added ions, the possibility of induced dipoles in the active molecule, or the possible screening or solvation of effective parts of the active molecule by molecules of the solvent. One might expect, however, for molecules where the negative charge is not adjacent to the asymmetric carbon atom, that the above series might remain approximately the same.

As an example of a simple ionised optically active compound, we may take the case of sodium mandelate, as investigated by Levene and Rothen (loc. cit.). The results are given in the following table:-

Salt added	n	$[M]_D^{25^\circ}$
LiCl	0.4	+ 180.2°
NaCl	"	+ 178.9°
KCl	"	+ 179.5°
Rb Cl	"	+ 179.2°
$CaCl_2$	"	+ 235.0°
$SrCl_2$	"	+ 197.2°
$BaCl_2$	"	+ 198.8°
-	-	+ 176.7°

n is the concentration of added salt in mols. per litre. The concentration of mandelate was in all cases approximately 0.05 M .

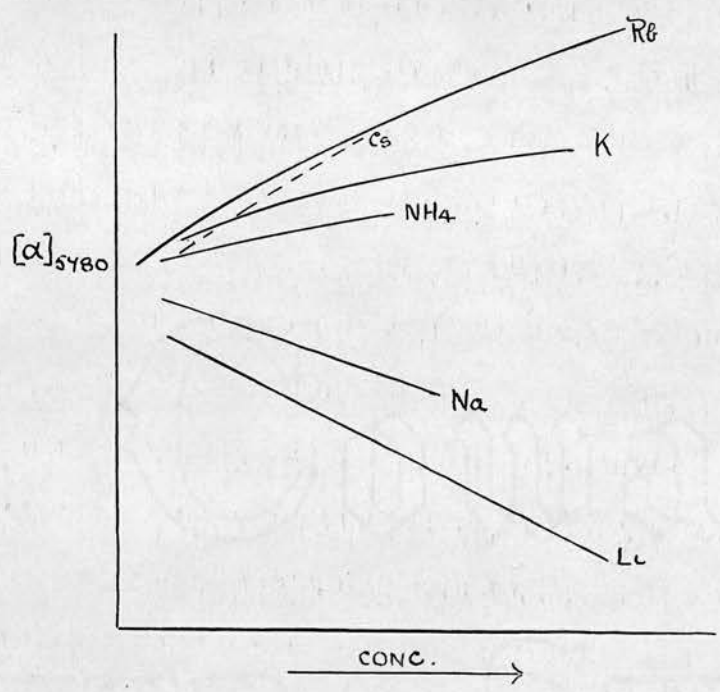
The addition of salts produces an increased absolute rotation in every case, the series of ion effects being given by

Ca^{++}, Ba^{++}, $Sr^{++} \gg Li^{+}$, K^{+}, Rb^{+}, Na^{+}.

The difference between the effect of the divalent and the monovalent ions is here of the order of 20°, apart from the exceptional elevation produced by Ca^{++}. This compares very favourably with the series (p. 12) found by the same authors for the unionised mandelic acid for which the differences between the divalent and monovalent metallic ions amounts to about 14°. It may thus be concluded that the salt effect has been disturbed to a small degree only by the ionisation of this comparatively simple active molecule.

A more complicated example is that of the tartrate ion, as illustrated by the aqueous solutions of tartrates of the alkali metals. Here we have the production of two negative charges in the same molecule on ionisation, and thus, on the basis cited above, one might expect additional complications, and, in particular, decided departures from the series of salt effects observed for the non-ionised compounds. Darmois (Ann. Phys., 1928, 10, 70; Trans. Far. Soc., 1930, 26, 384) found that on increasing the concentration/

concentration of the several solutions of the different alkali tartrates, the rotations of the sodium and lithium salts decreased, while those of the ammonium, potassium, rubidium and caesium salts increased, as shown by the following graphs:-



In accordance with the Oudeman Law, the rotation of all salts tends to the same value at infinite dilution. Darmois points out that the order of the curves in more concentrated regions, namely Li , Na , K , Rb , Cs , is the same as that of the ionic radii as calculated from ionic mobility. He concluded that the solvated lithium ion exerts a much smaller influence than the non-solvated caesium ion. He assumed that at the concentrations considered dissociation of the salt is complete, and that with increase in concentration/

concentration the tartrate ion undergoes a modification related to the radius of the cation. Since such a modification is taken as due to the electric field of the cation, it would be expected that this modifying effect would be greatest in the case of the smallest cations, namely Rb and Cs . It is then supposed that the increase in rotation in the cases of Rb, Cs, K and NH_4 is due to the preponderance of this deformation factor.

A second effect was, however, postulated by Darmois, since in the cases of lithium and sodium tartrates the rotatory power decreases with concentration. To account for this he assumed that the tartrate ion is hydrated in solution, and that the lowering effect is due to a dehydration of the ions by the positive ion. In the case of lithium and sodium, this dehydration effect is large enough to overcome the deformation effect. In support of this Darmois brings forward the results obtained with benzylamine tartrate and tetra-ethyl-ammonium tartrate. The former gives a rise in rotation with increasing concentration, in agreement with the fact that the benzylamine ion is not hydrated in solution. On the contrary, the tetra-ethyl-ammonium ion is hydrated, and the rotation shows a corresponding fall with increasing concentration. The effect of neutral salts on the rotation of sodium tartrate was also studied, the/

the results confirming the effects described above. Sodium and lithium chlorides produce a decrease in rotation while potassium chloride causes an increase. Magnesium chloride and calcium chloride cause a greater decrease than lithium chloride, this effect being accounted for by the dehydration theory. Similarly Long (Amer. Chem. Journal, 1883, 3, 351) found that potassium and ammonium halides raised the rotation of solutions of sodium and potassium tartrates, while sodium, lithium and thallium halides lowered it.

The dehydration theory advanced by Darmois has provoked some criticism. Thus Bancroft and Davies (J.P.C., 1930, 34, 897) state that the temperature changes accompanying the solution of tartaric or malic acids in water indicate no hydrate formation, while the molecular depression of the freezing point remains very constant and independent of increase of concentration of these acids. It is to be realised, however, that it is the acid and not the ion which is probably involved in these last determinations. On general grounds one would expect the tartrate ion, by virtue of its hydroxyl groups, to be hydrated to some extent at least. With a view to partially eliminating this factor, Rule and Hill (J.C.S., 1931, 2644,) studied the effect of salt addition on the rotation of a salt containing no hydroxyl groups, namely d-sec-β-octyl sodium phthalate. A water molecule can/

can be co-ordinated to another atom in two ways - either by the oxygen of the water acting as a donor, or by the hydrogen acting as an acceptor. While it is recognised that both anions and cations may be hydrated, it is generally concluded, from the greater co-ordinating power of oxygen in water, that the cations will hydrate more readily than the anions. In the case of d-sec-β-octyl sodium phthalate, therefore, it would be expected that the anion would be hydrated to a small extent only and any effects found must be due chiefly to the deformation of the anion. The results obtained may be arranged in a series similar to that already obtained in the case of non-ionised substances, the lowering due to the divalent cations being again more effective than that due to the monovalent. The authors point out, that in this deformation effect, not only the charge on the cation, but also its distance of approach, must be considered. The latter involves the consideration of the hydration of the cation. It would be expected that in the case of those cations, which are largely hydrated, the sheath of water molecules round the cation would act as a screen so that the deformation effect would be lessened. In agreement with this, it is found that the most highly hydrated ion (Li^+) exerts least effect, while the rubidium ion, for which hydration is least, has the greatest influence.

The above results of Rule and Hill show that the regularities/

regularities noted are not peculiar to compounds containing hydroxyl groups. This was later confirmed by Rule and Cunningham (loc. cit.) who obtained the same series for salt effect on dimethylene tartrate, dimethyl methylene tartrate, and methylene tartaric acid. The actual changes in rotation produced are smaller in the cases of dimethylene tartrate and dimethyl methylene tartrate, than in the case of methylene tartaric acid, where COOH groups are present with comparatively little ionisation, while a still greater effect is found with tartaric ester where hydroxyl groups are present. In all these compounds the normal series of salt effects is therefore observed. When, however, the negative charges are introduced by ionisation in, for example, solutions of di-sodium methylene tartrate, the order of cationic influence is again reversed.

It will be observed that the effects recorded in this section dealing with salt addition, have been regarded from the point of view, that the deformation of an optically active arrangement of atoms is, in the simple or normal case, due to the effect of the added cation on one attracting complex such as the hydroxyl group. The order of the series found is then in reasonable accord with expectations based on the degree of hydration and consequently the distance of approach of the cation. When, however, a second attractive/

attractive centre is introduced in the same molecule by ionisation, another effect may arise, which may counter-balance the change in rotation due to the previous one. This effect will be naturally greatest for those ions which are most accessible (the rubidium and caesium ions of the alkali metal series), and the net result may be the partial or complete reversal of the previous series effect.

In order to arrive at a more definite picture of the effects already mentioned, many attempts have been made to explain the physical basis of optical rotatory power. The idea that optical rotation is due to a coupling between the various resonators inside a molecule was first put forward by Born (Physikal Zeit., 1915, 16, 251; Ann. Phys. 1918, 55, 177) and Oseen (Ann. Phys. 1915, 48, 1). Later this was extended by others, more especially by Werner Kuhn (Zeit. Physik. Chem., 1929, B 4, 14; Trans. Far. Soc., 1930, 26, 293) who developed a model consisting of two resonators vibrating at right angles and separated by a definite distance. If there is no coupling between the resonators, each will vibrate independently, and there will be no optical activity. When a coupling does exist, the mode of vibration of each resonator is affected by the other, and it can be shown mathematically/

mathematically that the amount of energy picked up by the system of the two coupled resonators is different for d- and for l- circularly polarised light. In other words, the system will show optical activity. Kuhn concludes that if we can obtain an absorption band characterised by two components vibrating at right angles to each other as above, it will be found to be optically active. If the angle between the two vibrating components becomes less than 90°, the rotation will fall, until, when the vibrations are parallel, it becomes zero. Any factors affecting these vibrating components and their directions, will therefore produce a change in rotation. It is conceivable then that the effects of positive ions, dipoles etc., described above, can be explained on this basis.

Attempts have also been made to work out a theoretical formula giving the relation between the structure of the molecule and the magnitude of the rotation. Born and Oseen showed that in the case of a dissymmetric molecule, the ordinary refractive properties of the atoms will account for the rotation. On this basis, Gray (Phys. Rev., 1916, 7, 472) and de Malleman (Rev. gén. sci., 1927, 38, 453) calculated formulae for rotatory power, but the complexity of the expressions obtained render them of little practical use. More recently a formula has been worked out by Boys (Proc. Roy. Soc., A, 144, 655, 675; 1934) for a molecule/

molecule of the simplest asymmetric type i.e. with four different groups attached to one carbon atom. He takes as an analogy the case of rigid balls embedded in a gelatine gel, each ball corresponding to an atom. The optically active molecules, therefore, correspond to groups of such balls, each group consisting of four different balls situated at the corners of an irregular tetrahedron. Two kinds of model are thus present, related to each other as object to mirror image. The tetrahedral sets are distributed at random throughout the gel. Under the influence of a passing wave each ball vibrates and has an effect on the vibration of neighbouring balls. The secondary waves thus produced must be added to the original wave, and if the total effect of these is not in the same direction as the original wave, then the plane of polarisation of the original wave is rotated. In an analogous way, each atom in a molecule becomes an oscillating electric doublet under the influence of the electric field of the light wave. Allowing for the effect of such doublets on the field of the wave itself, and also on each other, the total polarisation of the molecule is calculated, and from this is derived the velocities of the two constituents of plane polarised light, namely d-circularly and l-circularly polarised light. The difference between these two velocities leads to the rotation. The following is the formula obtained:-

$$[\alpha] = \frac{72900\ (n^2 + 2)\ (n^2 + 5)\ R_A R_B R_C R_D\ I}{32\ \Pi^2 \lambda^2\ M\ N^3} \qquad (1)$$

where n is the refractive index of the medium in which the rotation is measured, R_A etc. are the total refractivities of each attached group, M is the molecular weight of the compound, N is Avogadro's Number, and I is a factor involving interatomic distances.

The above formula gives the contribution of a combination of four atoms to the total rotatory power, but Boys points out that the complexity renders the calculation impossible for common optically active substances. Also there is no way of finding accurately all the interatomic distances involved. In order to make the equation of practical use, it must be applied to a particular type of atomic structure so that its form becomes simpler, and the interatomic distances can be expressed in terms of some known property. Boys deduces such a simplified formula for the case of a compound containing four different radicals, when the radicals are small.

$$[\alpha] = \frac{C(n^2+2)(n^2+5)R_A R_B R_C R_D\ (1+F)(a-b)(a-c)(a-d)(b-c)(b-d)(c-d)}{\lambda^2 M\ (a+b+c+d)^{14}} \qquad (2)$$

n is the refractive index of the medium.
R_A etc. are the total refractivities of each attached group.
"a", "b", "c" and "d" are the effective radii of the groups in Ångström units, as calculated from their volumes.

C is a constant.

$F = f(\Delta a) + f(\Delta b) + f(\Delta c) + f(\Delta d)$

$f(\Delta a)$ etc. have not much effect on the numerical result.

The factor $(a-b)(a-c)(a-d)(b-c)(b-d)(c-d)$ is positive when $a > b > c > d$.

This formula, Boys applies to the calculation of the rotation of certain compounds, namely, amyl alcohol, amylamine, sec-butyl alcohol and sec-butylamine. In such cases the calculated rotation was in good agreement with that experimentally observed. It is interesting to note that the continued difference product in the equation recalls that previously suggested by Crum Brown (cf. p. 3).

It is thus seen that the above formula of Boys consists of three factors - $(n^2 + 2)(n^2 + 5)$, a property dependent on the medium in which the rotation is measured, $R_A R_B R_C R_D / \lambda^2$ dependent on the refractivities and the wavelength, and a third factor dependent on the spatial configuration. Changes in rotation may therefore be classified by considering the changes in these three factors.

From the simplified formula (2) it can be seen that any change in the effective radius of a group will produce a change in rotation, and if the effective radius of one group is gradually changed from a value greater to a value less than that of another group/

group then the rotation should change in sign (cf. Crum Brown). In support of this Boys cites the case of the optically active amyl derivatives:-

$$CH_3 - \underset{\displaystyle CH_2\,X}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - CH_2 - CH_3$$

Amyl alcohol (X = OH) and amylamine ($X = NH_2$) are found to have rotations in the opposite sense to all other compounds prepared by substituting various groups in place of X. In agreement with this, it is found that - OH and $-NH_2$ are the only radicals which have smaller atomic volumes than the $-CH_3$ group (i.e. $-CH_2X < -CH_2\,CH_3$), all the others causing $-CH_2X$ to be greater than $-CH_2\,CH_3$.

With this idea in mind, it is not difficult to explain the changes in rotation observed under certain conditions. If, for example, different polar groups are introduced into the optically active molecule, not only will the interatomic distances be affected by the difference in the actual size of the groups, but also the electric fields of the various dipoles will exert different deforming influences in the molecule. The greater the dipole is, the greater will be the deformation, and so the rotation, although dependent to some extent on the actual size of the substituent group, will also be determined by the magnitude of the dipole. Change of the interatomic distances by deformation/

deformation may be also brought about by the field of positive ions (cf. results of salt addition) or by the dipole of a polar solvent. In the latter case a second factor also comes in. If the solvent molecules associate with the solute, then the effective radius of the associating group in the solute will be altered. This also applies to the case in which the solute molecules associate with each other. Most of the results described under the headings, substitution effect, salt effect and solvent effect can, therefore, be explained by considering the changes brought about in the third factor I of Boys' equation.

Little work has been done with regard to the change in rotation with change in refractive index of the medium. Born and Oseen (loc. cit.) from their observations concluded that the molecular rotation is proportional to $(n^2 + 2)^2$; this relationship, however, was not confirmed by the results of other investigators. Gans (Ann. Phys., 1926, 79, 548) introduced theoretical corrections into the above, leading to the expression $[M] = k (n^2 + 2)$, a relationship which again was found to hold only in some particular cases. It is pointed out by Boys that any change in n would only produce a small change in the rotation, and it is only when variations, due to changes in the other factors, are absent, that this effect would become evident, as, for example, in the case of a non-polar compound where there is no tendency to co-ordinate/

co-ordinate even with a polar solvent. This is confirmed by the work of Rule and Chambers (Nature, 1934, Vol. 133, 910) who, in a study of the behaviour of the saturated hydrocarbon d-pinane towards change of solvent, found that the rotation is chiefly governed by the refractive index of the solvent medium.

It may be pointed out that the equation of Boys has been subjected to some criticism by Lowry and Allsopp (Proc. Roy. Soc., 1934, A 146, 300, 313). If change in the experimental conditions is limited to change in wave-length, then according to Boys' formula the change in optical rotatory power will depend on changes in the factor

$$(n^2 + 2)\,(n^2 + 5)\;R_A\,R_B\,R_C\,R_D/\lambda^2 \quad .$$

Thus, if the refractivities of the various groups are known, a value for the dispersion ratio for any two wave-lengths can be calculated. Lowry and Allsopp have estimated the refractivities of the groups involved in sec-butyl alcohol and act.-amyl alcohol, (regarding refractivity as an additive property), and have indicated that in these cases the equation of Boys does not yield an accurate value for the dispersion ratio. On the simple interpretation of Boys' equation, a zero rotation would be only obtained in such a case when one of the refractivities becomes zero, but the data of Lowry and Allsopp indicate that at an absorption band, where the rotation may pass through zero, the refractivity need not be zero, but may/

may show only a small variation from the values obtained in the transparent region.

To summarize, it may be stated that changes in optical activity are due to changes in the asymmetry of the molecule, brought about by alteration of its environment. The equation of Boys serves to correlate the majority of the results previously described, such results being explained by assuming changes in the factor I, brought about by deformation and association, including solvation. Thus substitution effect (Rule and co-workers) is explained by assuming deformation by the dipole, solvent effect (Rule and co-workers) by assuming deformation and association, and salt effect (Stubbs, Darmois etc.) by assuming deformation and possibly solvation.

In view of the fact that the presence of the - OH grouping in certain optically active substances has been associated with changes in association and molecular structure (notably in the tartaric acid series), with corresponding changes in rotation, the rotatory power of a compound containing no such groups was studied under various conditions. In this thesis, an account is first given of the optical rotatory powers of d-α-n-butyl-propionic acid and its methyl ester in various solvents, in relation to the refractive index of the medium and the polarity of the solvent. The investigation has been extended from inactive/

inactive solvents such as hexane, to ionising media such as aqueous and aqueous-alcoholic solutions. The rotatory powers of butyl-propionic acid and salts have been examined in relation to those of tartaric acid and its salts, with a view to correlating and contrasting results for the two series.

EXPERIMENTAL.

(a) Preparative.

Preparation of α-n-Butyl-Propionic Acid.

The above acid was prepared in the following stages:-

(I) n-Butyl-Malonic Ester (Ethyl)

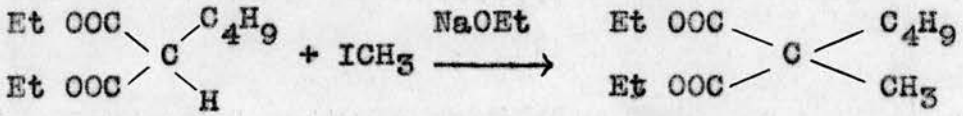
$$\begin{matrix} Et\ OOC \\ Et\ OOC \end{matrix}\!\!\diagdown\!\!\diagup CH_2 + Br\ C_4H_9 \xrightarrow{NaOEt} \begin{matrix} Et.OOC \\ Et.OOC \end{matrix}\!\!\diagdown\!\!\diagup CH.(C_4H_9)$$

A solution of sodium ethoxide was prepared by dissolving 77 grs. clean dry sodium in 1653 c.c. absolute alcohol (newly dried by refluxing over 1/20 of its weight of sodium and distilling into the flask in which it was to be used). This solution was shaken, cooled to about 50°C, and 515 c.c. ethyl malonate (freshly distilled B.D.H., B.p. 91-92°/19 mm.) slowly added. To the mixture, were added gradually 360 c.c. freshly distilled butyl bromide (B.D.H., B.p. 100°). The reaction commenced almost immediately, with the generation of considerable heat, sodium bromide being deposited. The mixture was then refluxed until neutral to moist litmus; this required about 4 hours. As much alcohol as possible was then distilled off on the water bath, and to the residue about 1340 c.c. distilled water were added, and the whole shaken thoroughly to dissolve the sodium bromide. The upper layer of n-butyl-malonic ester was separated and fractionated under diminished pressure in a Wittmar flask. First, a low boiling portion was obtained, consisting/

consisting of alcohol, water and butyl bromide, then a small intermediate fraction of unchanged malonic ester, and finally n-butyl-malonic ester boiling at 117-121°/ 12 mm.

Yield = 555 grs.

(II) Methyl-n-Butyl-Malonic Ester (Ethyl).



555 grs. butyl-malonic ester.

354 grs. methyl iodide.

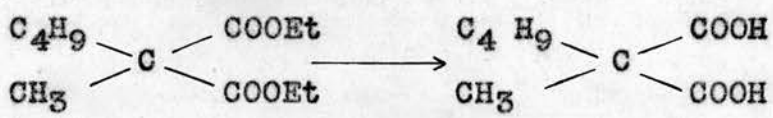
57 grs. sodium.

1247 c.c. absolute alcohol.

The reaction described above was again carried out using methyl iodide in place of butyl bromide and n-butyl-malonic ester instead of malonic ester. The methyl iodide was dried overnight over calcium chloride and fractionated before use (B.p. 42.5°) As before considerable heat was generated, the precipitated sodium iodide dissolved in water, and the crude ester separated. As there is very little difference between the boiling points of these mono- and di- alkylated malonic esters, separation by fractional distillation was not attempted.

Yield of crude ester = 537 grs.

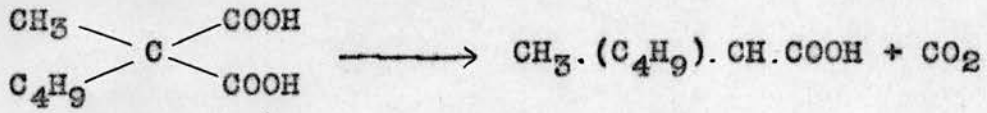
(III) Methyl-n-Butyl-Malonic Acid.



The disubstituted malonic ester (537 grs.) was hydrolysed by boiling under reflux overnight with 523 grs. potassium hydroxide (i.e. 4 molecular proportions - twice the equivalent amount) in aqueous alcohol, - 1700 c.c. alcohol : 425 c.c. water. This hydrolysis was carried out in two equal portions. The alcohol was then distilled off and water added to the residue, from which the acid was liberated by the addition of 20% sulphuric acid. The organic acid thus obtained separated as an oil, but on being stirred for a few minutes, it solidified. It was then extracted with ether, and the ether removed in a vacuum desiccator. A white solid was obtained, which was purified by dissolving in hot benzene, adding twice the volume of hot petrol ether (60°-80°), and leaving in a refrigerator for about one hour. After two such precipitations a clean substance of melting point 97° was obtained.

Yield = 327 grs.

(IV) <u>α-n-Butyl-Propionic Acid.</u>



The methyl-n-butyl-malonic acid was heated in an oil bath to 180° in a flask fitted with an inclined air condenser. There was a vigorous evolution of carbon dioxide, and when this had ceased the resulting monobasic/

monobasic acid was distilled under diminished pressure in a Wittmar flask.

Yield = 222 grs. boiling at 121°/19 m.m.

In order to avoid the use of recovered acid in the determination of the rotations, further preparations were carried out, resulting in an additional yield of 192 grs.

Total yield of acid = 414 grs.

Resolution of α-n-Butyl-Propionic Acid.

The quinine salt of the acid was formed by adding 316 grs. quinine (hydrated) to 110 grs. of the acid dissolved in 730 c.c. hot acetone. The quinine went into solution immediately and on cooling 280 grs. quinine salt crystallised out. The mixed salts were separated by repeated crystallisation from acetone. After the 5th, 6th and 7th recrystallisations, samples (3 grs.) of the salt were decomposed with 10% sulphuric acid (15 c.c.) and the free organic acid extracted with ether. The extract was washed with dilute sulphuric acid and water, dried over anhydrous sodium sulphate, and distilled in vacuo. Solutions of the acid in ethyl alcohol (c = 5) gave the following rotations:-

5th crystallisation $[M]^{20}_{5461} = 29.23^{\circ}$

6th/

6th crystallisation $[M]^{20}_{5461} = 31.34^{\circ}$

7th crystallisation $[M]^{20}_{5461} = 31.33^{\circ}$

The remaining quinine salt was then converted to the acid, as above.

Yield = 17 grs. boiling at $109^{\circ}/8$ mm.

The homogeneous acid gave a rotation of $[M]^{20}_{5461} = 30.52^{\circ}$ (cf. 29.04°, Rule and Smith, Thesis, Edin. Univ., 1932). In order to carry out further resolutions the quinine was recovered from the acetone residues as follows:-

Recovery of Quinine.

The acetone solution of quinine butyl-propionate was evaporated, and the resultant salt dissolved in dilute sulphuric acid. The organic acid thus liberated was extracted by means of ether, the quinine sulphate being precipitated by neutralisation of the excess sulphuric acid with ammonia. This was purified by recrystallisation from water. The free base was then obtained by adding concentrated ammonia to a boiling solution of the sulphate; this was filtered and washed with water. M.p. 176°.

An additional 36 grs. of butyl-propionic acid were obtained from these resolutions.

In ethyl alcohol (C = 5) $[M]^{20}_{5461} = 31.34^{\circ}$

(cf. 31.33° above)

Total yield of d- α -n-Butyl-Propionic Acid

= 53 grs.

Preparation of the Methyl Ester of d- α -n-Butyl-Propionic Acid.

26 grs. butyl-propionic acid

50 c.c. dry benzene

50 c.c. thionyl chloride

The thionyl chloride was slowly added to the benzene solution of the acid in a flask fitted with a ground-in condenser to which was attached a calcium chloride tube, and the whole was refluxed on a water bath until no more hydrogen chloride evolved. This required about 5 hours. The benzene and excess thionyl chloride were then distilled off on the water bath, and the crude acid chloride remaining was treated carefully with excess methyl alcohol, previously dried by sodium. This was again warmed under reflux for 1½ hours on the water bath, after which the excess methyl alcohol, benzene etc. were distilled off on an oil bath at atmospheric pressure. The remainder was fractionated under reduced pressure, a middle portion, 17 grs. (B.p. 63.5°/14 mm.: bath temperature 103°) being collected separately. The rotation of this was found in a 1 dm. tube:

$$\alpha^{20}_{5461} = 7.89\ (0)^{\circ}$$

The middle portion was again fractionated, first and last portions being rejected, and the rotation again measured.

Homogeneous/

Homogeneous $\alpha^{20}_{5461} = 7.88(7) = 7.89^{\circ}$

Yield = 15 grs.

Preparation of the Sodium Salt of d- α -n-Butyl Propionic Acid.

An ethyl alcohol solution of the acid was titrated with 2 N aqueous sodium hydroxide solution, phenolphthalein being used as external indicator. The bulk of the alcohol and water was distilled off in vacuo and the remainder removed in a vacuum desiccator. The salt was finally dried over calcium chloride and recrystallised from acetone. As it is deliquescent it was kept over calcium chloride, weighings being carried out as quickly as possible in a stoppered bottle.

Preparation of Ammonium Salt of d- α -n-Butyl-Propionic Acid.

As the sodium salt was used only in alcohol-water solutions, it was easily recovered by removing the solvents in a vacuum desiccator. From this the pure acid was obtained in the same way as from the quinine salt, i.e. the sodium salt was dissolved in dilute sulphuric acid, and the butyl-propionic acid thus liberated extracted with ether. The ether extract was washed with dilute sulphuric acid and water, and then/

then distilled in vacuo. An ethyl alcohol solution of the acid was then treated with excess ammonia (2 N). The resultant solution, after being filtered through a fine filter paper, was evaporated in a vacuum desiccator. It was found, however, that the salt obtained was too deliquescent to be kept dry for any time; it could not be dried by potassium hydroxide, while concentrated sulphuric acid took up the ammonia, thus liberating the acid.

TARTARIC ACID AND SALTS.

Tartaric Acid was obtained pure.
In water (c = 5) $[M]^{20}_{5461} = 23.70^{\circ}$ [cf. 23.50° (C = 5.1) Lowry and Austin, Phil. Trans. Roy. Soc. Lond., 1922, 222, 249].

Sodium and Ammonium Tartrates (Hopkin and Williams) were recrystallised from water, the former being kept for one day in an oven at 140° in order to drive off water of crystallisation (Pribram, Monats., 1898, 19, 172).
An aqueous solution of sodium tartrate (c = 5.124) gave a rotation $[\alpha]^{20}_{D} = 30.94^{\circ}$ [cf. 30.98°, (c = 5.122) Pribram, loc. cit.]
An M/2 solution of ammonium tartrate in water gave
$[\alpha]^{20}_{5780} = 35.44^{\circ}$

Thus $[\alpha]^{T''} = [\alpha] \times \frac{184}{148} = 44.1^{\circ}$

(cf. 44.6°, Darmois, Ann. Phys., 1928, 10, 70)

Tetra-Ethyl-Ammonium Tartrate.

A solution of exactly 14 grs. of tetra-ethyl-ammonium bromide in methyl alcohol was added to the equivalent amount of freshly prepared moist silver oxide (precipitated by sodium hydroxide from the equivalent amount of silver nitrate in aqueous solution, and thoroughly washed). The precipitated silver bromide was filtered off, and the filtrate titrated with/

with aqueous tartaric acid solution, using phenolphthalein as external indicator. The solution was evaporated in a vacuum desiccator, and the resultant solid dried over calcium chloride until of constant weight. As it is deliquescent, it was kept over calcium chloride.

Urea, as supplied by Kahlbaum, was used.

Glycerol was fractionated under reduced pressure before use. B.p. 170°/8 mm.

(b) Purification of Solvents.

All solvents used were specially purified, the methods adopted for purification being described briefly in the following pages:-

(1) Acetic Acid. Kahlbaum's 100% acetic acid was cooled until about two-thirds frozen; the liquid portion was decanted off and the crystalline mass fractionated. M.p. 16° ; B.p. 118-118.2°.

(2) Acetone. B.D.H. "bisulphite purified" acetone was well dried over anhydrous calcium chloride and fractionated. B.p. 55-56°.

(3) Acetonitrile. Aytoun, Scott and Co's acetonitrile was dried over calcium chloride and fractionated, giving a colourless product, B.p. 80.7 - 81.4°.

(4) Acetophenone. Merck's acetophenone was partially crystallised and the crystalline portion filtered off, dried and fractionated. M.p. 20°: B.p. 201.8 - 201.9°.

(5) Aniline. Kahlbaum's aniline "from sulphate" was dried and fractionated giving a colourless liquid of B.p. 182.9 - 183°.

(6) Anisole. B.D.H. anisole was washed with sodium hydroxide solution and water, dried and fractionated. It was colourless and gave no phenol reaction. B.p. 153.8°

(7) Benzene. B.D.H. "extra pure" benzene was partially frozen out and the solid mass dried and fractionated/

fractionated. F.p. 5.5° ; B.p. 80 - 80.1°

(8) Benzonitrile. Aytoun, Scott and Co.'s product was dried and partially frozen out; the crystalline portion was fractionated under reduced pressure. It was obtained as a colourless liquid of F.p. - 12.9° and B.p. 82.5°/15 mm.

(9) Carbon Disulphide. Aytoun, Scott and Co.'s redistilled carbon disulphide was shaken with mercury to remove sulphur, dried over calcium chloride and repeatedly fractionated. B.p. 46 - 46.2°.

(10) Carbon Tetrachloride. The sample used had already been carefully purified. It was dried and fractionated. B.p. 77.6 - 77.8°.

(11) Chlorobenzene. The B.D.H. product was washed with sodium carbonate and water, dried over anhydrous calcium chloride and fractionated. B.p. 131.6 - 132°.

(12) Chloroform. Aytoun, Scott and Co.'s chloroform was shaken with concentrated sulphuric acid for ¼ hour to remove alcohol. It was then washed with sodium hydroxide solution and water, dried over anhydrous potassium carbonate and fractionated. B.p. 60.7 - 60.9°. This method is due to Hentzsh and Hoffmann (Ber. 1911, 44, 1777).

(13) Cyclohexane. B.D.H. cyclohexane was dried, partially frozen out, dried and fractionated. M.p. 4.1° ; B.p. 80.1 - 80.3°.

(14) o- Dichlorobenzene. On cooling B.D.H. o-dichlorobenzene to - 20°, a small amount of crystalline substance/

substance (probably p-dichlorobenzene) was deposited, and rapidly filtered off at the pump. The liquid was then dried over calcium chloride and fractionated under reduced pressure. B.p. 60 - 61°/11 mm.

(15) Ethyl Alcohol. "Absolute" ethyl alcohol was refluxed with $\frac{1}{20}$ of its weight of sodium, and then fractionated. B.p. 78°.

(16) Hexane. B.D.H. hexane ("free from aromatic hydrocarbons") was dried and fractionated. B.p. 67-69°.

(17) Iodobenzene. The B.D.H. product was washed with sodium carbonate solution and water, dried over calcium chloride and fractionated. It was obtained practically colourless. B.p. 75°/16 mm.

(18) Methyl Alcohol. "Absolute" methyl alcohol was purified according to the method of Bjerrum and Zichmeister (Ber. 1923, 56, 897). The alcohol was allowed to stand in a reflux apparatus with clean dry magnesium (10 grs. to each litre). A vigorous reaction set in and the alcohol boiled. When all the metal had disappeared, the mixture was refluxed for 4 hours and then distilled (first and last fractions being rejected) in a current of dry air.

(19) Methyl Iodide. Hopkin and Williams' methyl iodide was washed with sodium carbonate solution and water, dried over calcium chloride and fractionated. B.p. 41.8 - 42°.

(20) Methylene Chloride. The B.D.H. product was washed with potassium hydroxide solution and water, dried/

dried over calcium chloride and fractionated. B.p. 41.8 - 42.2°.

(21) Methylene Iodide. The B.D.H. product was washed with sodium hydroxide solution and water, dried over anhydrous sodium sulphate, and fractionated in vacuo. This was shaken with mercury and filtered before use. B.p. 70°/11 mm.

(22) Nitrobenzene. B.D.H. nitrobenzene was fractionated and the portion boiling at 205.5° partially frozen out. The crystalline portion was melted, dried over calcium chloride, and fractionated under reduced pressure. F.p. 5.6 - 5.7°. B.p. 92°/15 mm.

(23) Nitromethane. The B.D.H. product was washed, dried over calcium chloride and fractionated. It was obtained colourless. B.p. 100.8 - 101.1°.

(24) n-Propyl Alcohol. The B.D.H. product was refluxed over freshly prepared lime and then fractionated. B.p. 97°.

(25) Toluene. Aytoun, Scott and Co.'s "pure" toluene was dried with sodium wire and fractionated. B.p. 109.7 - 109.8°.

(c) Determination of Optical Rotatory Power.

The polarimeter was a Hilger instrument provided with a Lippich three-shadow polarizer, and two verniers reading to 0.01°. A quartz mercury vapour lamp was used as the source of light for the mercury green line, this line being almost exclusively used in the determination of rotations. The temperature of the room was maintained at $20^{\circ}C$ ($\pm$ 0.2°), and all solutions were also made up at this temperature.
The average of ten readings was taken for each rotation.

Refractive Index Measurements.

The refractive indices of solutions of the methyl ester of butyl-propionic acid were measured for the Na_D line by means of a Pulfrich Refractometer, each solution being water-jacketed to $20^{\circ}C$.

(TO FACE PAGE 46)

TABLE I.

Methyl α-n-Butyl-Propionate in Methane Solvents.

T = 20° l = 4 dm.

Solvent	grs. ester per 100 c.c. soln.	α^{20}_{5461}	$[M]^{20}_{5461}$	n_D	$\mu \times 10^{18}$ e.s.u.
CH_3OH	4.999	+ 2.05°	+ 14.7(7)°	1.3312	1.68
CH_3CN	4.999	2.04	14.6(9)	1.3460	3.21
CH_3COCH_3	5.002	1.97	14.1(8)	1.3589	2.84
CH_3COOH	5.000	1.90	13.6(8)	1.3715	1.40
CH_3NO_2	5.002	1.89	13.6(0)	1.3813	3.05
C_6H_{14}	5.001	1.84	13.2(4)	1.3760	0.00
* Homogeneous	87.68	7.89	12.9(6)	1.4083	1.80
CCl_4	5.002	1.80	12.9(5)	1.4607	0.00
Cyclohexane	5.000	1.76	12.6(7)	1.4273	0.00
$CHCl_3$	5.001	1.76	12.6(7)	1.4464	1.10
CH_2Cl_2	4.998	1.73	12.4(6)	1.4237	1.61
CS_2	4.999	1.73	12.4(6)	1.6276	0.00
CH_3I	5.002	1.57	11.3(0)	1.5293	1.35
** CH_2I_2	5.004	0.66	9.5(0)	1.7559	1.08

* l = 1 dm. ** l = 2 dm.

EXPERIMENTAL RESULTS AND DISCUSSION.

Examination of the Boys formula for the rotation of an optically active substance, indicates that in the absence of variation due to all other factors the rotation ought to be proportional to $(n^2 + 2)(n^2 + 5)$, where n is the refractive index of the medium. Strictly speaking this would then refer to a non-polar substance dissolved in non-polar inert solvents. While the following results were obtained for an ester, for which the measured dipole moment is approximately 1.8×10^{-18} e.s.u., yet they are of considerable interest in this connection.

The optically active substance was the methyl ester of d- α-n-butyl-propionic acid: details of the rotations found with various solvents are given in Tables 1, 2, and 3, the arrangement being in the order of decreasing rotatory powers.

(Table I opposite)

In this table, $[M]^{20}_{5461}$ is the recorded molecular rotation at 20°C. for the mercury green line for solutions in the solvents given in the first column. Corresponding values of the dipole moments, as determined by the ordinary experimental methods (cf. Trans. Far. Soc., 1934, 30), and the refractive indices for Na_D light of the pure solvents, are given under the headings μ and n_D respectively. Strictly speaking, comparison/

comparison should be made with values of the refractive index for the green line 5461, but these were not obtainable in every case; the differences involved are very small, being of the order 0.004, and do not affect the series order. The concentration of ester was in all cases almost exactly 5 grs. per 100 c.c. of solution. It is to be noted that in Boys' equation $\underline{n}$ refers to the refractive index of the solution, not the solvent, but the difference involved is again small, and does not involve any changes in the relative magnitudes.

Examination of the table then shows a definite relationship between refractive index and molecular rotation, in the sense that, generally, the rotation decreases as the refractive index increases. At the same time, the dipole moment of the solvent has possibly an appreciable effect, as is shown by the general trend of the figures in the table, and in particular by the results for nitromethane and hexane, where the higher dipole moment of the former may conceivably account for the fact that the nitromethane solution shows a higher rotation than corresponds to its refractive index. It would therefore appear that the final rotation in each case is mainly the result of a balance between these two tendencies - the effect of a highly polar solvent tending to raise, and the effect of a highly refractive one tending to lower the rotation. This is more readily seen by comparing,

for/

for example, the two very similar non-polar solvents, hexane and cyclohexane. In this case the only effect is that due to the different refractive indices; and cyclohexane with the higher refractive index gives a lower rotation. Again, on comparing acetic acid and hexane, the solution in the polar solvent, acetic acid, has a greater rotatory power than would be expected from the very small difference in the values of n.

what about CCl_4 and cyclohexane?

It is interesting to note that the rotatory power of the ester in the homogeneous state falls into a position in the table, in excellent agreement with the refractive index of the liquid. Esters as a class do not undergo appreciable association - as tested by the usual methods - and there is no evidence that the close proximity of the polar ester molecules in the homogeneous liquid here results in any marked upward displacement in rotatory power. Further information on this point is discussed later in connection with concentration experiments (p. 55).

An abnormality of the above table is the position of carbon bisulphide. The high value of its refractive index leads to the expectation of a lower rotation than that actually observed. On the basis of the foregoing discussion, an upward displacement of rotation might be anticipated with solvents of a strongly polar character, and although carbon bisulphide is non-polar with respect to its behaviour in a uniform electric field, it has been emphasized

by/

by Rule and McLean (J.C.S., 1931, 674) that the molecule contains two strong and mutually compensating dipoles. It is therefore possible, that under conditions such as the present, one of these dipoles (that nearer to the dipoles in the active molecule) is involved in the electrical deformation of the active compound. The solvent thus behaves as if it were of polar type. A similar suggestion has been advanced by the above authors to explain the behaviour of methyl l-menthyl naphthalate in carbon bisulphide solution, and shown to account for the much larger polar influences exerted by p-disubstituted benzenes of the type $O_2N.C_6H_4.NO_2$, for which μ also is zero. In the present instance, however, it would be necessary to assume that carbon bisulphide produces an even greater deformation than the polar methyl iodide, which is just below it in the table. Such an assumption appears improbable, and it is possible that refractive index and polarity are not the sole factors governing the solvent effect. Nevertheless, it remains a significant factor that the parallel between the values of [M] and n is also subject to minor displacements in the cases of the halogen derivatives, carbon tetrachloride, chloroform, and methylene chloride, all of which are built up of two or more dipoles. These chlorine derivatives arrange themselves in such a way that the least refractive methylene chloride yields the/

the lowest rotation, and the most highly refractive carbon tetrachloride the highest value, the values of n thus running in the opposite direction to the main trend of the table.

TABLE 2.

T = 20° l = 4 dm.

Solvent	grs. ester per 100 cc. soln.	α^{20}_{5461}	$[M]^{20}_{5461}$	n_D	$\mu \times 10^{18}$ e.s.u.
CCl_4	5.002	+ 1.80°	+12.9(5)°	1.4607	0.00
$CHCl_3$	5.001	1.76	12.6(7)	1.4464	1.10
CH_2Cl_2	4.998	1.73	12.4(6)	1.4237	1.61

These divergencies cannot be explained by assuming carbon tetrachloride to exert a polar influence, since the latter would in any case be smaller than the influence of methylene chloride or chloroform. We can only conclude from Table I that a general relationship appears to exist between the refractive index of the solvent and the rotatory power of the solution, and that the individual character and electrical structure of each solvent also exerts its own influence upon the rotation.

Further evidence of two main opposing factors is given for a series of solvents of the benzene type, the results of which are given in Table 3. With the aromatic/

(TO FACE PAGE 51)

TABLE 3.

Methyl α-n-Butyl-Propionate in Benzene Solvents.

T = 20° l = 4 dm.

Solvent	grs. ester per 100 cc. soln.	α^{20}_{5461}	$[M]^{20}_{5461}$	n_D	$\mu \times 10^{18}$ e.s.u.
$C_6H_5NO_2$	5.000	+ 1.95°	+ 14.0(4)°	1.5529	3.90
C_6H_5CN	5.000	1.94	13.9(6)	1.5278	3.84
C_6H_6	5.003	1.88	13.5(3)	1.5014	0.00
C_6H_5Cl	5.002	1.86	13.3(9)	1.5250	1.56
$o\text{-}C_6H_4Cl_2$	5.000	1.84	13.2(4)	1.5490	2.24
$C_6H_5NH_2$	5.000	1.84	13.2(4)	1.5863	1.60
C_6H_5I	5.000	1.81	13.0(3)	1.6180	1.25
$C_6H_5CH_3$	5.001	1.80	12.9(6)	1.4955	0.40
$C_6H_5OCH_3$	5.000	1.80	12.9(6)	1.5164	1.25
$C_6H_5COCH_3$	4.999	1.80	12.9(6)	1.5332	2.97

aromatic solvents, however, the total variation in refractive index is relatively small, and the corresponding variations in rotatory power amount to little more than 1°. The solvents are arranged arbitrarily in the table to illustrate the discussion more clearly.

(TABLE 3 opposite)

It will be observed that the two solutions in nitrobenzene and benzonitrile stand by themselves, giving much higher rotations than the remaining compounds. These two liquids are also by far the most polar of the liquids examined. The central section of the table contains five solvents for which a rising refractive index goes hand in hand with a decreasing rotation.

The last three solvents, toluene, anisole and acetophenone, are exceptional, and do not fall into line with those in the central section. Each of these three liquids givesa solution of the same rotatory power, namely $[M]^{20}_{5461} = 12.96°$, and if we disregard their position with respect to the other aromatic liquids under examination, we may arrive at a partial explanation of their optical behaviour, by considering that these similar rotations are the result of two opposing factors. On the one hand, there is a tendency for the rotation to increase as we pass from toluene to acetophenone, owing to the rise in the polarity of the/

10. Patterson & Anderson, J., 1912, 101, 1633. Effect of salts on levulinic acid & on levulinic ester.

$Ba^{++} >> K^+ > Na^+ > NH_4^+$ OH Interaction? not ionisation

11. Levene & Rothen, J. Phy. Chem., 1930, 34, 2567.
Mandelic acid
~~$Ba^{++} >> K^+ > Na^+$~~
Ba - Sr - Ca > K - Na - Li OH Interaction (confirmed by ester, el. etc. replacing OH)

13. malic acid (Stubbs, J., 1911, 99, 2165).
$Cs^+ > Rb^+ > K^+ > Na^+ > NH_4^+ > Li^+ > H$.
$Ba^{++} > Ca^{++} > Mg^{++} > Cd^{++} > Al^{+++} > Zn^{++} > Hg^{++}$

14. Rolla & Bruningham (J.) & methylene lactonic acid & its dimethyl ester
14. sodium mandelate (Levene & Rothen)
$Ca^{++} > Ba^{++} > Sr^{++} > Rb^+ - K^+ - Na^+ - Li^+ > H$

15. Darmois, Ann. Phys. 1928, 10, 70.
Trans. Far. Soc., 1930, 26, 334
Verification of Ordelmann's Law. a.c.j.
(1) Ionic hydration cf. Long (J. Chem. S., 1883, 3, 357)
(2) Deformation Bruneau (J. Phy. Chem., 1930, 34, 897)

16. Rolla & Hill, J., 1931, 2624.
Sod. ethyl phthalate h. OH

[Summary p. 24]

Ionisation. Is it really a factor
and displacements of $OH^- + Na^+ \rightarrow ONa + H^+$

Thio Thesis

Butyl-propionic acid. Varnish solvent
hexane ether aq. ether aq. alcoholic + salt: cl

Carpet.

31. α-n-Butyl propionic ester (Reference

36. Tribel

37. Na salt

39. Tartaric acid

41. Solvents

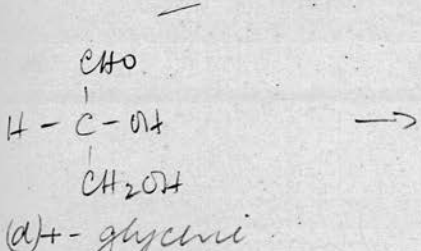
46. Refractometer

52 Condensation

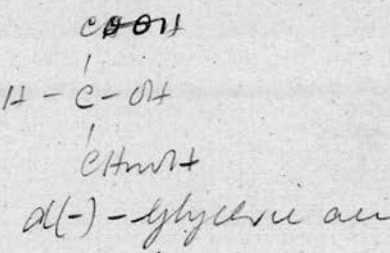
Highly Refractive, high Boiling
Dipole, low volatile

---

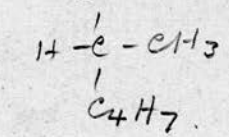
p. 50.



(d)+ - glyceric aldehyde



d(-) - glyceric acid



the medium, but on the other hand, this is counter-balanced by the fall in rotation corresponding to the rise in refractive index. The marked difference between the behaviour of the two non-polar liquids, benzene and toluene, is a curious point. It must also be noted, that in spite of the fact that all the solvents of the benzene type have a greater refractive index than the solute, all the rotations in these solvents are either the same, or greater than the value for the homogeneous ester. It may be mentioned that the rotations in benzene, hexane and cyclohexane decrease progressively and correspond to a progressive increase in the refractivities $\left\{R = \frac{(n^2 - 1)}{(n^2 + 2)} \cdot \frac{M}{d}\right\}$

The reverse relationship is reported for the acid chloride of α-bromocamphor - Π- sulphonic acid in various solvents by Walden (Monats. 53, 36, 1929); but attempts to establish a correlation between the rotations given for methyl butyl-propionate in Tables 1, 2 and 3 and the refractivities of the corresponding solvents, lead to many discrepancies.

Despite the small range of rotation values given by the aromatic solvents, it may still be concluded that the experimental data afford further support for the existence of two main influences: an increasing polarity of solvent leading to a rise in the dextro-rotation, and an increasing refractive index producing the opposite change.

The concentration curves of the above ester in certain solvents are of considerable interest in view of the above general conclusions. Considering the question from the refractive index point of view, it is evident that, as the concentration of ester decreases by the progressive addition of solvent to the homogeneous ester, the refractive index of the solution changes from that of the ester itself to the limiting case of that of the solvent (infinite dilution). If then, two inert solvents are chosen such that the refractive index of the ester lies between the two indices of the solvents, the changes in refractive index of the solutions with dilution will be in opposite directions, and we should expect the molecular rotation of the optically active substance to show corresponding variations. The rotations of solutions of the methyl ester of d- α -n-butyl-propionic acid were therefore examined for various concentrations in the solvents, hexane and cyclohexane, both of zero dipole moment and of refractive indices 1.3760 and 1.4273 respectively. The refractive index of the homogeneous ester is 1.4083. Results are given in Fig. I, where the molecular rotation and the refractive index of the solution are plotted against the number of moles of solvent per mole of solute. The refractive indices and rotations of the various solutions are given in Tables 4 and 5.

TABLE 4.

Methyl α-n-Butyl-Propionate in Hexane. T = 20°

ℓ	grs. ester per 100 cc. soln.	Mols. solvent / Mol. ester.	α^{20}_{5461}	$[M]^{20}_{5461}$	n_D (soln)
1	87.68	0.0	+ 7.89°	+ 12.9(6)°	1.4083
2	10.13	9.7	1.88	13.3(7)	1.3819
4	5.001	20.9	1.84	13.2(4)	1.3794
4	2.504	43.0	0.94	13.5(2)	1.3770

TABLE 5.

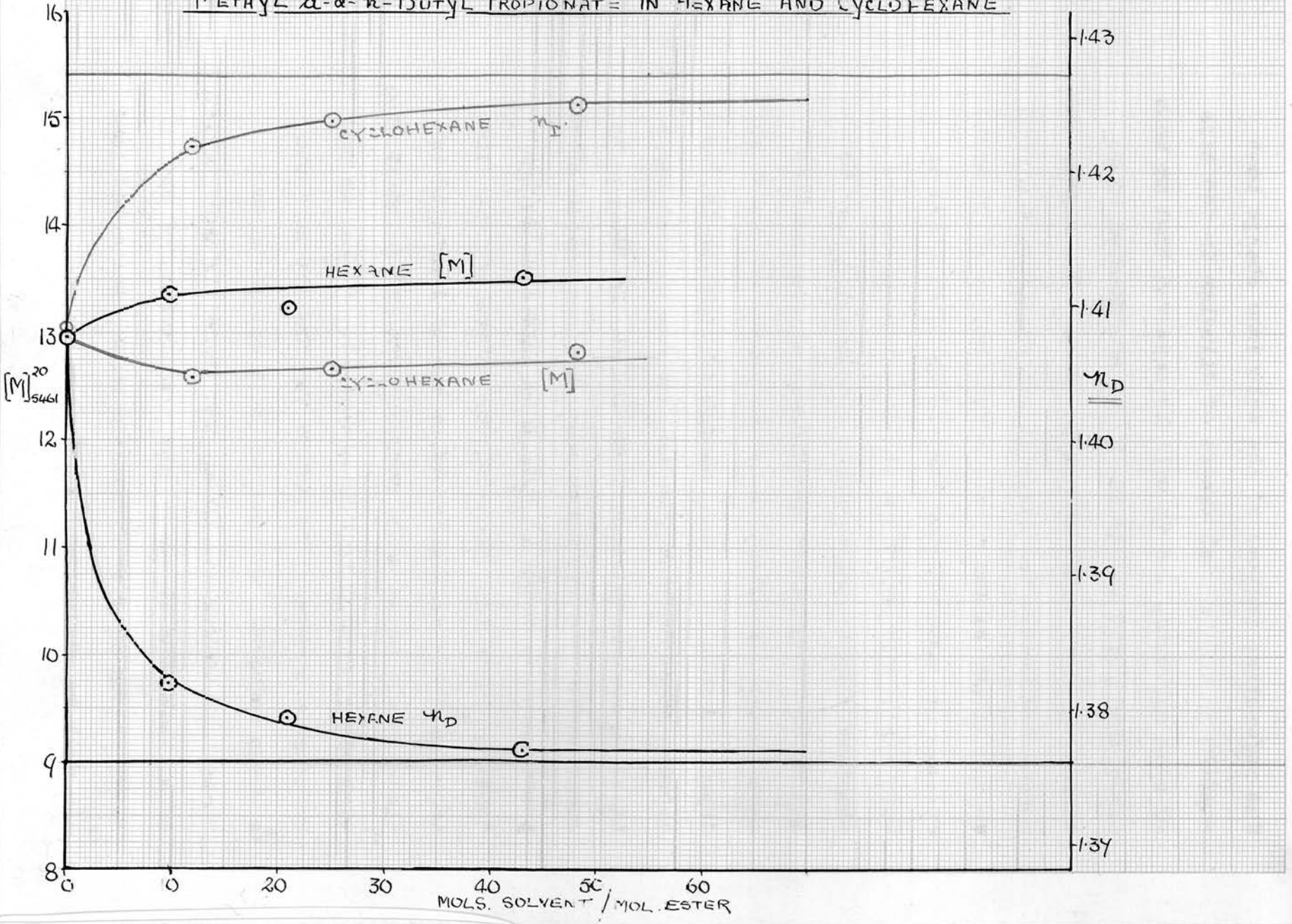
Methyl α-n-Butyl-Propionate in Cyclohexane. T = 20°

ℓ	grs. ester per 100 cc. soln.	Mols. solvent / Mol. ester	α^{20}_{5461}	$[M]^{20}_{5461}$	n_D (soln)
1	87.68	0.0	+ 7.89°	+ 12.9(6)°	1.4083
2	9.954	11.9	1.74	12.5(9)	1.4219
4	5.000	25.0	1.76	12.6(7)	1.4238
4	2.667	48.3	0.95	12.8(2)	1.4250

(TO FACE PAGE 55)

Fig. 1

METHYL d-α-n-BUTYL PROPIONATE IN HEXANE AND CYCLOHEXANE



The refractive indices of the solutions change most rapidly in the initial stages of dilution in the case of both solvents, and it will be observed that in both cases this rapid change in $\underline{n}$ is accompanied by a correspondingly rapid change in $[M]$. The higher the refractive index, the lower is the rotation, and vice versa. Above values of the concentration of 10 mols. solvent per mol. solute, the change in rotation is very small, corresponding to little change in refractive index: any possible change would then be due to the progressive breaking-up of the possible ester-ester complexes, formed by reason of the ester dipole moment. That the changes of rotation in the initial stages of dilution are not due to this cause is shown by the opposite direction of the changes in rotation for the two solvents. From the tables given previously, it is to be concluded that association tends to raise the rotation, the effect of this being especially noticeable for solutions of the ester in the strongly polar media nitrobenzene and benzonitrile, with which it will tend to associate. So far as can be judged, however, the curves for the two solvents are approximately symmetrical with regard to the changes in refractive index, and hence the association, or at least the change in the association, of the ester molecules with themselves under such conditions can only be regarded as small.

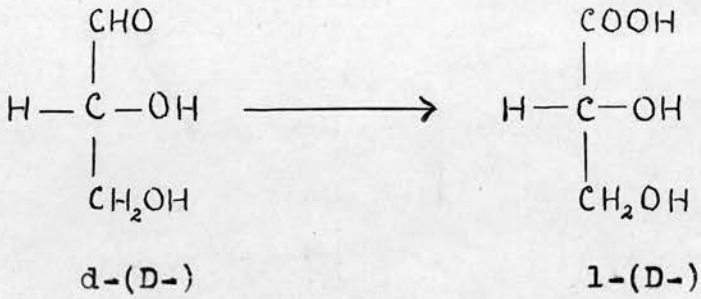
The previous results are thus regarded as definitely establishing a distinct relationship between refractive index and molecular rotation, although in general the changes in rotation found in this connection are small. This is in agreement with the general equation of Boys. It remains to discuss the fact that this equation predicts a rise in rotation for a rise in refractive index $\{[M] \propto (n^2 + 2)(n^2 + 5)\}$, whereas for the above ester the converse is the case. At the same time, it is to be noted that association with a solvent dipole tends to raise the rotation, an effect which again is in opposition to the usual experience (Introduction p. 6).

In discussing this question, it is convenient to consider the relationships in the group of substances represented by tartaric acid, glyceric acid and α-n-butyl-propionic acid. All three acids are distinguished by the possession of the atom arrangement $R_1CH\ R_2\ COOH$, where the space relationships of these component radicals are of the greatest importance from the point of view of establishment of the configuration of the molecules concerned.

It is well known that dextrorotatory (d)-glyceric aldehyde on oxidation gives laevorotatory (l)-glyceric acid, but, as pointed out by Freudenberg (Stereochemie (1932) p. 668 et seq.), to both these d- and l-

compounds/

compounds the same space configuration D- is attributed



d-(D-) 1-(D-)

The D-configuration is assigned to the l-acid for two main reasons. Firstly, the esters and salts of the l-acid are all dextrorotatory; secondly the acid has the same configuration as the first three atoms of the dextrorotatory gluconic acid (which on the basis of its sugar relationship has a D-configuration) and as both halves of *d*-tartaric acid (Freudenberg, loc. cit. p.668-9).

In the particular case of dextrorotatory α-butylpropionic acid we have as yet no definite information bearing upon its configuration. Levene and his coworkers (Cent., 1932, I, 40; 1933, I, 1277) have made a number of configurational studies with acids of this type, but so far only with a view to determining the relationships existing among acids of the acetic acid series, in which no substituent other than an alkyl group is present. Considering the strongly modifying influence exerted by polar substituents such as - OH and - O CH_3 upon the optical properties of these acids, it is not possible to rely upon comparisons between/

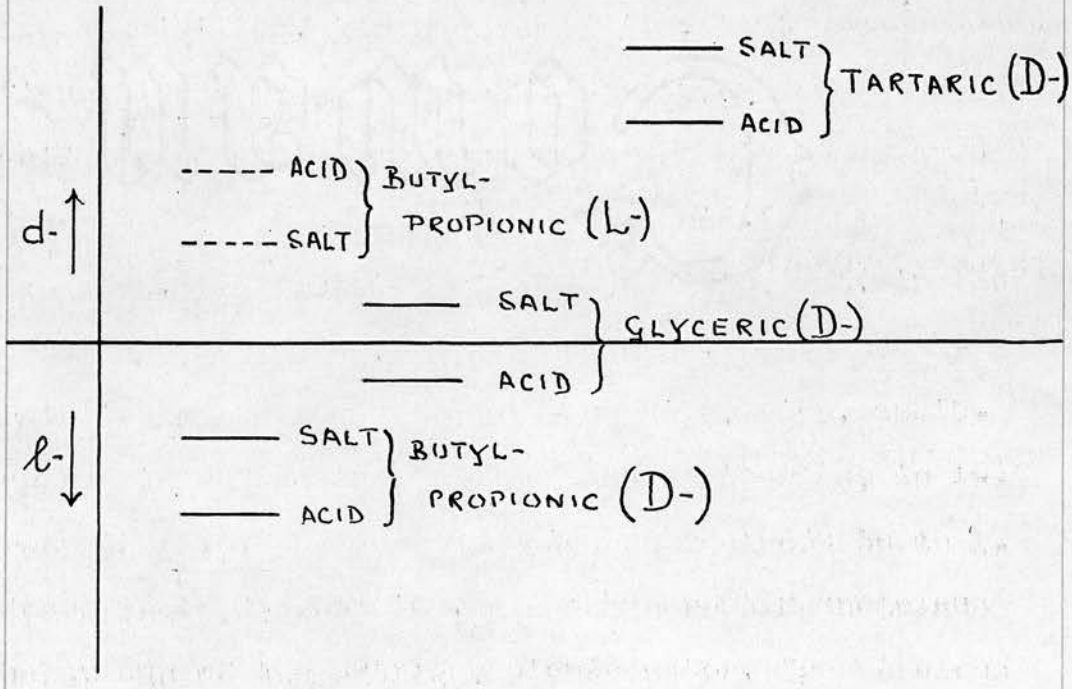
between the acetic acid series and that of the hydroxy acids discussed above. Attention may however be drawn to several interesting points of analogy between α-butyl-propionic acid and glyceric acid. As will be shown later the salts and methyl ester of d- α - butyl-propionic acid have lower rotations than the free acid, that is, esterification and ionisation displace the rotatory power towards the laevo-direction. In this respect the acid resembles d-glyceric acid (L-configuration), although in the latter case the displacement is so marked that there is an actual change of sign from dextro- to laevo- . There remains the possibility, if not probability, that a close configurational resemblance exists between these two acids and that the compound under examination may be described as d-L-butyl-propionic acid.

Now, the equation of Boys predicts that, in the case of a normal asymmetric molecule, where the l- rotation corresponds to an L- configuration, an increase in refractive index causes an increase in l- rotation i.e. an increase which corresponds to a decrease in d- rotation. The apparently anomalous behaviour of the butyl-propionic ester, from the refractive index point of view, is then regarded as due to the fact that the dextro- rotation is associated with an L- configuration. The fact that the rotation in various solvents increases with increasing dipole moment of the solvent is again contrary to the usual rule (cf. Rule and co-workers), and is to be/

be explained on a similar basis.

At this stage we may conveniently summarise the relative rotations of the undissociated acids, tartaric, glyceric, and butyl-propionic, together with those of the respective highly ionised salts. It is well known that the salts of d-tartaric acid show a higher rotation than the d- acid itself, while the salts of l- glyceric acid have a d- rotation; in both instances the rotation of the acid, considered from the dextro- side, is lower than that of the salt, while all are considered to have a D- configuration.

Fig. 2.



The diagram (Fig. 2) brings out very clearly the resemblance between l- butyl-propionic acid and l-D-glyceric acid, which has been emphasized above.

d-α-*n*-BUTYL-PROPIONIC ACID - CONCENTRATION CURVES.

In the following section, the conclusions derived in the previous pages concerning the influence of refractive index and polarity of the solvent on the optical rotatory power of the methyl ester of n-butyl-propionic acid, have been applied to the case of similar solutions of the free acid.

Rule and Smith (Thesis, Edin. Univ., 1932) found that in acetone, hexane, and benzene, the rotation fell progressively as the concentration of this acid increased, but in the case of ether, a definite maximum was observed, which was not easily explained on the same principles as the other curves. The results of Rule and Smith for these solvents have been embodied in Fig. 3; further data for ethyl and n-propyl alcohols were now obtained and are given in Tables 6 and 7. The acid, employed in these alcohol solutions, had a slightly higher rotation in the homogeneous state than that used by the above authors. The values in the two alcohols have therefore been lowered by multiplying by the factor 0.952 (cf. discontinuous curves) in order to show their relative positions with regard to the data of the other solvents.

TABLE 6./

TABLE 6.

d- α -n-Butyl-Propionic Acid in Ethyl Alcohol. T = 20°

ℓ	grs. acid per 100 cc. soln.	Mols. Alcohol / mol. acid.	α^{20}_{5461}	$[M]^{20}_{5461}$
0.5	91.50	0.0	+ 10.74°	+ 30.5(2)°
2	32.30	4.5	15.30	30.7(8)
2	19.97	8.8	9.57	31.1(4)
2	11.13	17.7	5.35	31.2(5)
2	5.000	42.9	2.41	31.3(3)

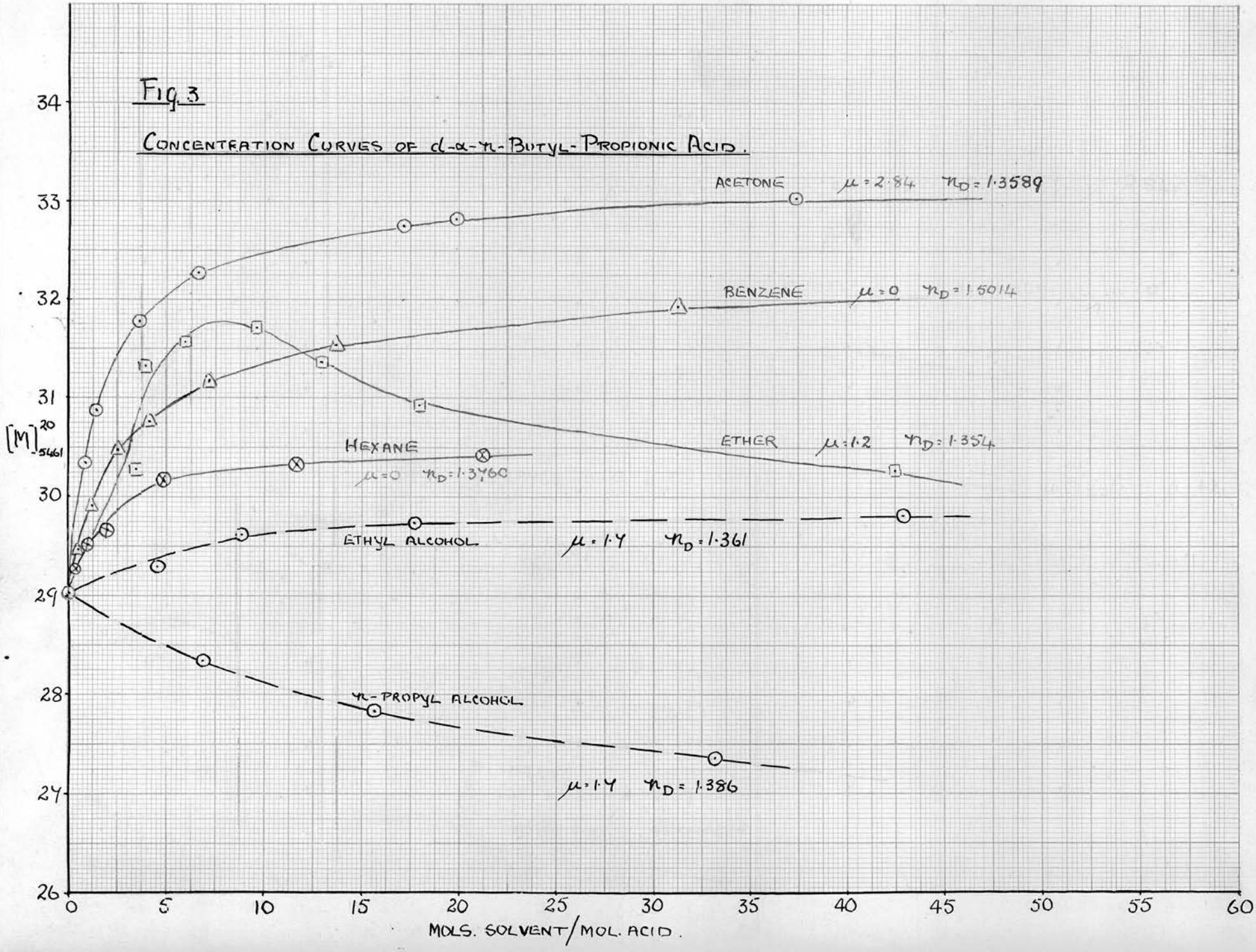
TABLE 7.

d- α -n-Butyl-Propionic Acid in n-Propyl Alcohol. T = 20°

ℓ	grs. acid per 100 cc. soln.	Mols. Alcohol / mol. acid.	α^{20}_{5461}	$[M]^{20}_{5461}$
0.5	91.50	0.0	+ 10.74°	+ 30.5(2)°
2	20.00	6.8	9.17	29.8(0)
2	9.998	15.6	4.50	29.2(5)
2	4.996	33.1	2.21	28.7(6)

Fig. 3

CONCENTRATION CURVES OF d-α-n-BUTYL-PROPIONIC ACID.



It is seen that the concentration curve in acetone is of the same type as that obtained for the methyl ester in hexane. The initial rise in rotation can therefore be taken as due, partly at least, to the initial sudden fall in the refractive index of the solution, [n_D acid = 1.4198 n_D acetone = 1.3589] this effect gradually falling off as the dilution increases. The polarity of the solvent must also be taken into consideration. The fact that the curve for acetone, the most strongly polar solvent of the series, occupies the highest position, indicates that association of the acid molecules with those of the solvent leads to a higher rotation, as in the case of the methyl ester. This is confirmed by considering the rotations at various concentrations in ethyl alcohol, a solvent with approximately the same refractive index (n_D = 1.361), but with a smaller dipole moment. The curve obtained is of the same type but lower down in the series.

A second complication is introduced by the association of the acid molecules with themselves, which is generally recognised as taking place to a considerable extent in that class of substances. If there were no such association, then all the curves (for solvents with less refractive index than the homogeneous acid) would show a rise, on dilution, to final values, all greater than the homogeneous value and determined/

determined by the refractive indices and dipole moments of the various solvents. The fact that, from a general view-point, the acid must be taken as associating with itself, leads to a value for the experimentally determined homogeneous rotation, higher than is consistent with its refractive index (n_D = 1.4198), and it is therefore conceivable that such a value may be greater in some cases than the rotation at infinite dilution. If dissociation of the acid-acid complexes does not appreciably occur in the region where the refractive index undergoes its marked change, then the form of the curve will correspond to that obtained in the case of ether as shown in Fig. 3. The initial rise is then regarded as due to the effect of the low refractive index of the solvent (n_D = 1.354). The ether, however, breaks up the association complexes of the acid, and a lowering of the rotation then results. This explanation is supported by polarisation measurements of acetic acid in various solvents. Thus Wolf and co-workers (Phys. Zeit., 1930, 31, 227) from measurements in very dilute solutions in non-polar solvents, calculated a dipole moment of 0.74×10^{-18} e.s.u., while the same measurements made in dilute ether solution gave $\mu = 1.4 \times 10^{-18}$ e.s.u. (Smyth and Rogers, J.A.C.S., 1930, 52, 1824). Since the latter value corresponds to that obtained from measurements in the vapour state at low pressures, it is probable that this is the true value for the unassociated molecule/

molecule. It thus appears that ether is efficient in breaking up the association complexes of the acid, without itself associating with the acid molecules so liberated. In the cases of acetone and ethyl alcohol already described, such solvent-solute complexes are formed, so that the rotation does not fall.

All values recorded for n-propyl alcohol solutions are less than the value for the homogeneous acid. It therefore appears probable that n-propyl alcohol, like ether, breaks up the association of the acid, and that the possible effect of the solvent dipole, which would tend to raise the rotation, is small. The relative position of the curve as a whole is consistent with its high refractive index (n_D = 1.386).

It remains now to consider the non-polar solvents, where there can be no association with the solute. The curve for hexane, as far as obtained above, does not show a falling off as might be expected on increasing dilution with a non-polar solvent. This would then indicate that hexane, in the case of the above acid, is not a particularly efficient separator of the acid-acid complexes at these concentrations. It is indeed a matter of general knowledge that the saturated aliphatic hydrocarbons and benzene are not specially efficient in separating such acid complexes, as judged by molecular weight determinations in such solutions: for example Amvers (Zeit. phys. Chem., 1893, 12, 689) found that n-caprylic acid had a molecular/

molecular weight of double the normal value even in a 2% benzene solution. At infinite dilution in hexane, however, where separation of association complexes is presumably complete, one would expect the rotation to fall below the corresponding rotation in ethyl alcohol solution, by reason of refractive index and dipole moment considerations.

The curve for benzene in Fig. 3 is abnormal in that all values in the range of concentrations studied are higher than the homogeneous acid value, in spite of the higher refractive index of the solvent (n_D = 1.5014). This is then probably related to the results for the methyl ester in the benzene group of solvents, where the group as a whole is associated with higher values of the rotation, although the influences of refractive index are visible in that group. It may be noted that the polarisation curves of various alcohols diluted with benzene show a maximum at an intermediate concentration (cf. Introduction p. 9), but comparable figures for acid and ester in benzene are not available.

It will be shown later that ionisation of α-n-butyl-propionic acid is accompanied by a decrease in rotation. Assuming then a rough analogy between the ionising power of a solvent and its dielectric constant (cf. Walker, Introduction to Physical Chemistry, 1927, p. 299), the high value of the rotation in/

in benzene might have been correlated with the low dielectric constant of this solvent. The fact that the rotation of the methyl ester, however, has a similarly higher value in benzene seems to render this explanation improbable. In the discussion above, the possible changes in ionisation in the different solvents are regarded as having negligible effects on the relative values of the rotations.

AQUEOUS-ALCOHOLIC SOLUTIONS OF d-α-n-BUTYL-PROPIONIC ACID.

The concentration curves of n-butyl-propionic acid in various solvents have been explained by considering the effects brought about by association of the acid, either with itself or with the solvent, and by the change in refractive index. A lowering of the refractive index and an increase in association both tended to give a rise in rotation. It would therefore be expected that water, by virtue of these two factors at least, would produce a corresponding increase. Since the acid does not dissolve in water alone, the effect of its addition to alcoholic solutions of the acid was studied. The alcohols employed were ethyl and n-propyl, the results being given in Tables 8 and 9, and represented graphically in Fig. 4. In each case results were obtained for three different concentrations of optically active solute (c = 5 , 10 and 20).

In accordance with Fig. 3, the relative values of the rotations in ethyl alcohol solutions are in the reverse order to those in n-propyl alcohol.

Examination of Fig. 4 shows that in all cases addition of water causes a fall in rotation, notably rapid/

TABLE 8.

d-α-n-Butyl Propionic Acid in Ethyl Alcohol-Water Mixtures.

$T = 20^{\circ}$

ℓ	grs.acid per 100 cc. soln.	Molar % H_2O in Solvent.	α^{20}_{5461}	$[M]^{20}_{5461}$
2	5.000	0.0	+ 2.41°	+ 31.3(3)°
2	5.002	10.8	2.39	31.0(6)
4	4.997	37.6	4.65	30.2(4)
4	4.997	54.7	4.60	29.9(1)
4	5.000	72.1	4.49	29.1(9)
4	5.001	82.1	4.40	28.5(9)
2	11.13	0.0	5.35	31.2(5)
2	10.00	35.4	4.63	30.1(0)
2	10.00	59.1	4.47	29.0(6)
2	10.00	77.2	4.34	28.2(1)
2	19.97	0.0	9.57	31.1(4)
2	20.00	24.8	9.30	30.2(3)
2	20.00	44.9	9.05	29.4(1)
2	20.00	64.1	8.72	28.3(4)
2	20.00	73.6	8.54	27.7(6)

TABLE 9.

d- α -n-Butyl-Propionic Acid in n-Propyl Alcohol-Water Mixtures.

$T = 20^{\circ}$

ℓ	grs. acid per 100 cc. soln.	Molar % H_2O in Solvent.	α^{20}_{5461}	$[M]^{20}_{5461}$
2	4.996	0.0	+ 2.21°	+ 28.7(6)°
2	5.002	4.7	2.20	28.5(9)
4	5.002	19.0	4.31	28.0(0)
4	5.001	32.8	4.21	27.3(5)
2	5.004	70.4	2.00	25.9(8)
2	9.998	0.0	4.50	29.2(5)
2	10.00	11.0	4.46	28.9(9)
2	10.00	19.9	4.42	28.7(3)
2	10.00	38.9	4.28	27.8(2)
2	9.998	52.6	4.19	27.2(4)
2	9.998	69.7	4.07	26.4(6)
2	20.00	0.0	9.17	29.8(0)
2	20.00	16.4	8.98	29.1(9)
2	20.00	38.3	8.73	28.3(7)
2	20.00	54.5	8.49	27.5(9)

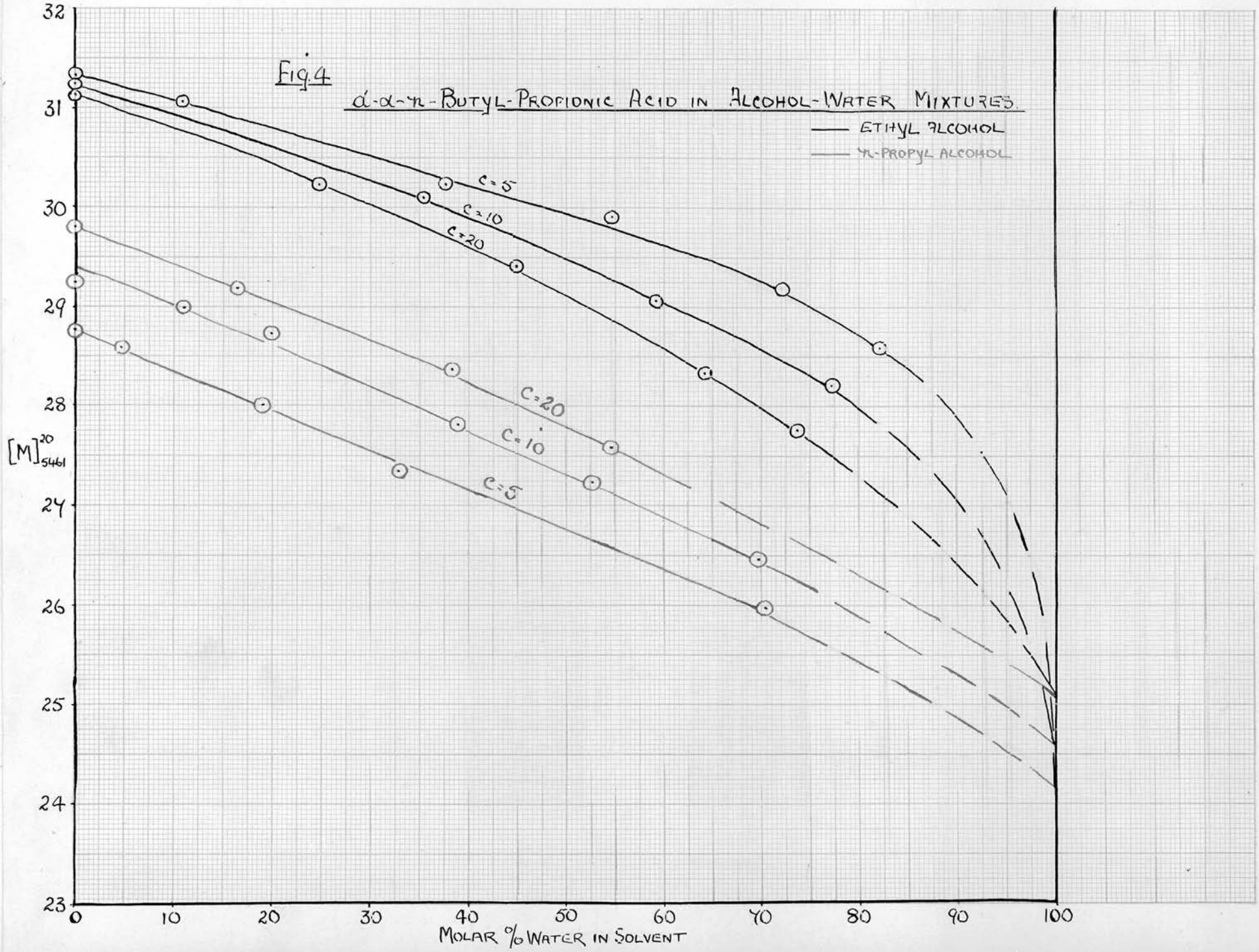


Fig. 4
α-α-n-Butyl-Propionic Acid in Alcohol-Water Mixtures.
Ethyl Alcohol
n-Propyl Alcohol
c=5
c=10
c=20
c=20
c=10
c=5
[M]$^{20}_{5461}$
32
31
30
29
28
24
26
25
24
23
0
10
20
30
40
50
60
70
80
90
100
Molar % Water in Solvent

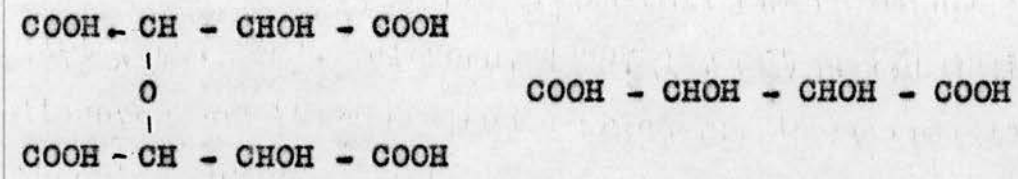
rapid when the percentage of alcohol is relatively small. A similar rapid change in such regions has been cited for ammonium α-bromocamphor-Π-sulphonate in aqueous-alcoholic mixtures by Campbell (J.P.C., 1931, 35, 1143). In the present case, the effect is contrary to that expected from dipole moment and refractive index considerations. It may therefore be concluded that such a decrease is due to some factor peculiar to water and not introduced by the other solvents used. The most probable explanation is then that on the addition of water, the acid is progressively ionised, the rotation of the ion being less than that of the undissociated acid. This ionisation effect must be sufficiently great to overcome the other factors operating in the reverse direction. Such being the case, it would be expected that in aqueous solution, the more dilute solutions, where ionisation is relatively greater, would have the lower rotations; the ethyl alcohol curves would then cross before they reach the axis for pure water (cf. discontinuous curves of Fig. 4). Correspondingly, the rotation of a dilute aqueous solution of a salt such as sodium butyl-propionate, where dissociation is complete and where the dilution is such that the rotation will be unaffected by the positive ion, would be still further below these values on the water axis. The concentration curve for sodium butyl-propionate in/

in water (Fig. 6(a) later) shows that such a value is approximately 21^{o}, and thus offers no opposition to this expectation.

TARTARIC ACID.

The rotatory dispersion of tartaric acid has been the subject of numerous investigations since Biot (Mem. Acad. Sciences, 1838, 15, 93) reported the discovery of its anomalous character; in general the theories put forward in explanation, have been based upon the interpretation of Arndtsen (Ann. Chim. et Phys., 1858, 54, 403) that there are simultaneously involved two normal dispersions, which are dextro- and laevo- rotatory respectively, and of which the difference under the given conditions, gives rise to the observed anomaly. Thus, the remarkable variations in rotatory power of aqueous solutions of the acid with change in concentration have come to be regarded as due to changes in chemical structure of the acid. A further extension of these ideas is summed up in the statement that just as the optical activity itself of organic compounds is a property of the molecule rather than of the crystal, so also the variation in rotation of tartaric acid solutions as well as the anomalous rotatory dispersion is molecular in character, in the sense that it is due to the co-existence in solution of at least two different types of molecule. Thus de Mallemann (J. Physique, 1923, VI, 4, 18) concluded that in all aqueous solutions containing neutral salts, tartaric acid was a mixture/

mixture of two forms of the following formulae:-



Similarly Lowry and Austin (Nature 114, 431, 1924) have tentatively suggested that two structures similar to the two alternative formulae for dimethylene tartrate may perhaps prove the key to the problem.
Now, all such formulae depend for their formation on the presence of the hydroxyl grouping, by co-ordination or by direct chemical action: and therefore the behaviour of tartaric acid under conditions approximating to those under which rotations of α-butylpropionic acid (cf. p. 67) were examined, has been here investigated and reported on in the following pages.

TABLE 10.

Tartaric Acid in Ethyl Alcohol - Water Mixtures.

$T = 20^{\circ}$

ℓ	grs. acid per 100 cc. soln.	Molar % H_2O in Solvent	α^{20}_{5461}	$[M]^{20}_{5461}$
4	5.000	0.0	$+ 0.64^{\circ}$	$+ 4.8(0)^{\circ}$
4	5.000	15.2	0.66	4.9(5)
4	5.000	27.7	0.69	5.1(7)
4	5.000	51.0	0.92	6.9(0)
4	5.000	68.2	1.32	9.9(0)
4	5.000	79.1	1.80	13.5(0)
4	5.000	100.0	3.16	23.7(0)
2	9.999	0.0	0.66	4.9(5)
4	10.00	36.3	1.64	6.1(5)
4	10.00	51.9	2.06	7.7(3)
4	10.00	79.2	3.57	13.3(9)
2	9.999	100.0	2.98	22.3(5)
4	20.00	46.4	3.30	6.1(9)
4	20.00	52.0	3.73	6.9(9)
4	20.00	77.0	6.23	11.6(8)
4	20.00	89.7	8.86	16.6(2)
4	20.00	100.0	10.87	20.3(8)

TABLE 11.

Tartaric Acid in n-Propyl Alcohol - Water Mixtures.

$T = 20^{\circ}$

ℓ	grs. acid per 100 cc. sol^{n}.	Molar % H_2O in Solvent.	α^{20}_{5461}	$[M]^{20}_{5461}$
4	5.000	0.0	+ 0.06°	+ 0.4(5)°
4	5.000	25.6	- 0.14	- 1.0(5)
4	5.000	43.1	- 0.08	- 0.6(0)
4	5.000	65.8	+ 0.35	+ 2.6(3)
4	5.000	82.6	+ 1.12	+ 8.4(0)
4	5.000	92.0	+ 2.07	+ 15.5(3)
4	5.000	100.0	+ 3.16	+ 23.7(0)
4	10.00	34.6	- 0.05	- 0.1(9)
4	10.00	39.4	+ 0.01	+ 0.0(4)
4	10.00	55.1	+ 0.38	+ 1.4(3)
4	10.00	85.1	+ 2.63	+ 9.8(6)
4	10.00	86.7	+ 2.84	+ 10.6(5)
4	10.00	93.0	+ 4.23	+ 15.8(6)
2	9.999	100.0	+ 2.98	+ 22.3(5)
4	20.00	47.1	+ 0.40	+ 0.7(5)
4	20.00	69.0	+ 2.23	+ 4.1(8)
4	20.00	82.9	+ 4.44	+ 8.3(3)
4	20.00	96.7	+ 9.54	+ 17.8(9)
4	20.00	100.0	+ 10.87	+ 20.3(8)

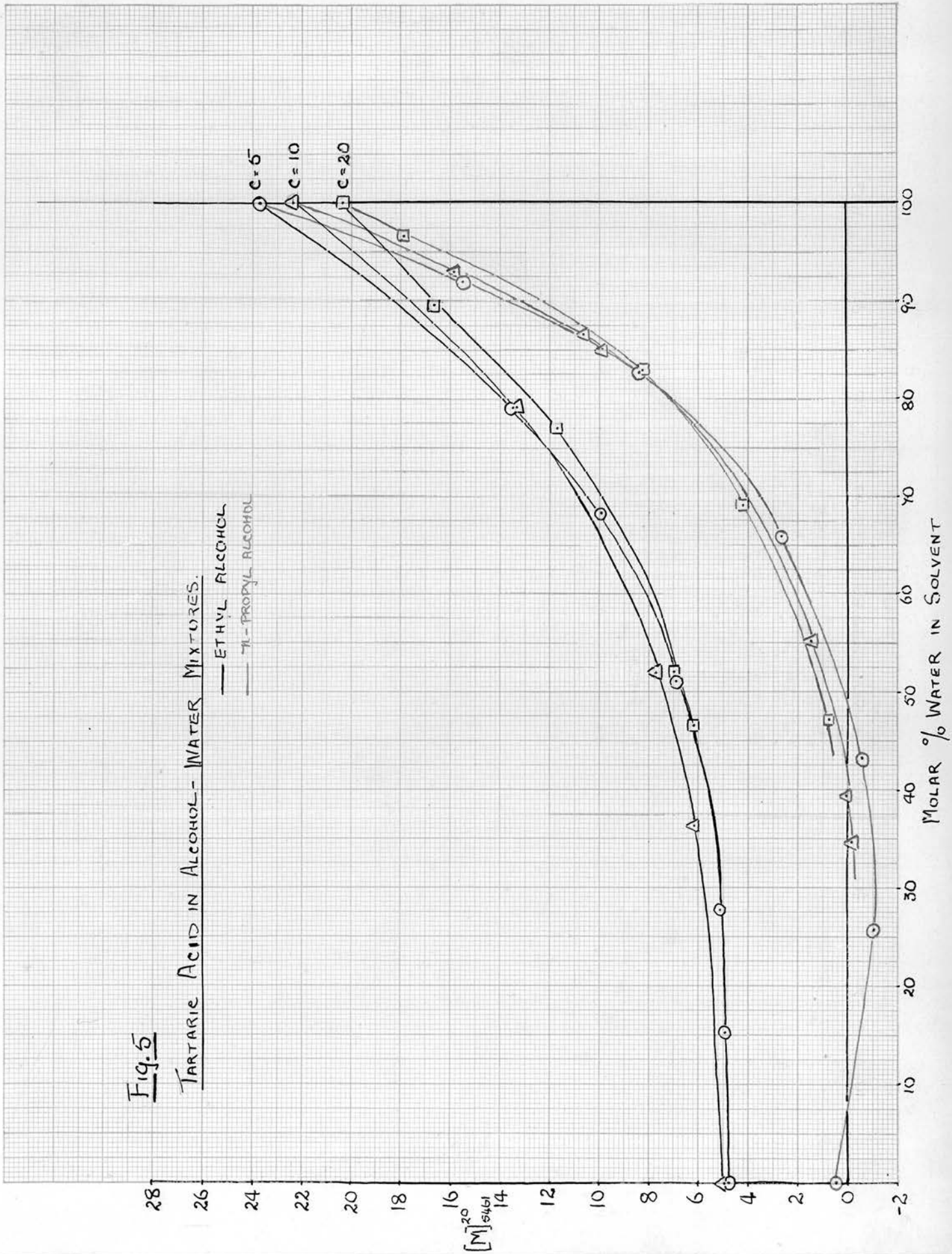


Fig. 5

Tartaric Acid in Alcohol-Water Mixtures.

In Fig. 5 and Tables 10 and 11 are shown the changes in rotation produced by the addition of ethyl and n-propyl alcohols to aqueous solutions of tartaric acid of various concentrations viz. c = 5, 10 and 20. In some cases the low solubility of the acid in the alcohols concerned did not permit of values being obtained in alcohol-rich mixtures, but, in general, the main trend of the curves can be followed.

In comparing such curves for tartaric acid with those obtained under similar conditions with butyl-propionic acid (Fig. 4) it must be remembered that the latter acid, while exhibiting a d-rotation is assumed to have an L - configuration (cf. p. 58). Since an L - configuration is normally associated with an l - rotation, it would be well in a comparison involving butyl-propionic acid to consider all the rotations of this acid from the laevo-side. Thus it is evident that the changes in rotation must be considered as acting in the reverse direction, an apparent fall being really a rise, and vice versa.

In the case of butyl-propionic acid it was deduced (p. 70) that, since the ion has a lower dextro-rotation than the undissociated acid, the rotation in aqueous solution would fall on dilution, or, if considered on the above basis, a rise would be obtained. Similarly, it is found that the rotation of tartaric acid in water also rises with dilution.

Also/

Also it was found that the rotations of butyl-propionic acid in propyl alcohol were above those in ethyl alcohol (considered from the laevo-side), this being regarded as due simply to differences in refractive index and effective dipole moment. In opposition to this, tartaric acid exhibits lower rotations in propyl alcohol, and moreover, the difference in this case is much too large to be explained by changes in the above factors. The effect produced by the difference in refractive index would be small, and when applied to low rotations, as in the present case, its relative influence would be negligible. Similarly the large change cannot be explained from the dipole moment point of view. A possible explanation lies in the fact that certain non-aqueous solvents exhibit ionising properties. As pointed out by Nernst and J.J. Thomson such ionising power is related to the dielectric constant of the solvent; the higher the value of the latter, the feebler is the attraction between oppositely charged particles immersed in that solvent. The following table gives the dielectric constants of various solvents:-

H_2O	81
CH_3OH	33.7
C_2H_5OH	25.7
C_3H_7OH	21.8
$CH_3CO\ CH_3$	21.4

It/

It is thus probable that tartaric acid ionises to a greater extent in ethyl than in propyl alcohol, so that a greater rotation is obtained.

The extent to which tartaric acid shows ionisation compared with butyl-propionic acid depends on the character of the acids themselves;as far as has been ascertained, the dissociation constant of the latter acid has not been measured. Tartaric acid, by virtue of its hydroxyl groups will have a greater tendency to associate with the various solvents. From the view, supported by Walker (Introduction to Physical Chemistry, 1927, p. 299) and Kendall (J. Amer. Chem. Soc., 1917, 39, 2303, 2323; 1921, 43, 1416; 1922, 44, 717) that combination between solvent and solute precedes ionisation, it can be understood that tartaric acid would ionise to a greater extent than butyl-propionic in the above solvents. In comparing the rotations of butyl-propionic acid, in ethyl and propyl alcohols, therefore, the ionisation factor does not come in to any great extent (cf. p. 66).

It would be expected that the order of dielectric constants given above would be the same as that of the rotations of tartaric acid in the various solvents,

$$[M]_{H_2O} > [M]_{CH_3OH} > [M]_{C_2H_5OH} > [M]_{C_3H_7OH} > [M]_{CH_3COCH_3}$$

if the ionisation factor is the main one. This order is borne out by the results of Winther (Zeit. phys. Chem. 1902, 41, 183).

Since/

Since tartaric acid would be expected to ionise more readily in ethyl than in propyl alcohol, the latter would give the more normal curve, considered apart from ionisation. The addition of water to such solutions will therefore be considered first.

As can be seen from Fig. 5 the first additions of water produce a fall in rotation, negative values being obtained. As however, the proportion of water is increased further, the first effect is superceded by a second, which causes a rise in rotation. This change is rapid in the region of relatively small alcohol percentage, a feature already noted in the corresponding case of α-n-butyl-propionic acid (p. 70). For reasons similar to those given above for pure alcohol solutions, the effect of change in refractive index would be very small and within the limits of experimental error. It is possible, however, that the initial lowering is due to the effect of the dipole of the added water. When however sufficient water is present the ionisation effect will become predominant and the rotation will rise as the degree of ionisation increases. The quantitative relationship between ionisation (to the ions H^+ and HT^-) and rotatory power of aqueous solutions of tartaric acid, has been demonstrated by Britton and Jackson (J.C.S., 1934, 998). In the case of the ethyl alcohol curves, the ionisation effect is sufficient/

sufficient to obscure the initial dipole effect.

The order of rotations of tartaric acid in pure alcohol can be explained by the principles previously discussed (p. 60 et seq) only if the changes in ionisation involved by altering the dilution of the acid, are negligibly small. This appears to be the case as the curves cross over in a manner similar to the ethyl alcohol- water curves of butyl-propionic acid. It is significant that the proportion, water : alcohol, at which these intersections occur, is, as would be expected, greater for the less ionising propyl alcohol than for ethyl alcohol.

SALTS OF BUTYL-PROPIONIC AND TARTARIC ACIDS.

(a) Sodium d- α -n-Butyl-Propionate.

The case of the salts of the acids would be expected to be more complicated than that of the acids themselves, as in addition to dipole effects we now have complications due to the large degree of ionisation. Also variations in the degree of ionisation as for example with change in concentration, although themselves small, would produce a noticeable effect, because of the large difference in rotation between the ion and the undissociated acid.

Refractometric and light absorption data (Fajans 1927; Von Halban, 1928) favour the view that, contrary to the initial postulate of the Debye-Hückel theory, even strong electrolytes contain a definite proportion of "undissociated" molecules; the fraction of associated ions is given as roughly more than five per cent in aqueous solutions of concentration greater than 5 N (cf. Glasstone, Recent Advances in Physical Chemistry, 1931, p. 411). The factors tending to cause an increase in the proportion of undissociated molecules or of associated ions are just those which are responsible for the tendency of an electrovalency to pass over into a covalency, and so the relative sizes and charges of cation and anion must be considered in deciding on the possibility of partial dissociation/

(TO FACE PAGE 82)

TABLE 12. Sodium Butyl-Propionate in Water. T = 20°

l	grs. salt per 100 cc. soln.	Molar Conc.	α^{20}_{5461}	$[M]^{20}_{5461}$	
4	1.010	0.067	+ 0.55°	+ 20.7°	
4	1.246	0.082	0.66	20.1	
4	1.504	0.099	0.79	20.0	
4	1.880	0.124	0.97	19.6	
4	2.413	0.159	1.20	18.9	

TABLE 13. Sodium Butyl-Propionate in Ethyl Alcohol. T = 20°

l	grs. salt per 100 cc. soln.	Molar Conc.	α^{20}_{5461}	$[M]^{20}_{5461}$	
4	3.800	0.250	+ 0.86°	+ 8.6°	
4	5.700	0.375	1.23	8.2	
4	7.599	0.500	1.49	7.4(5)	
4	10.27	0.680	1.75	6.4(5)	

TABLE 14. Sodium Butyl-Propionate in n-Propyl Alcohol. T = 20°

l	grs. salt per 100 cc. soln.	Molar Conc.	α^{20}_{5461}	$[M]^{20}_{5461}$	
4	3.801	0.250	+ 0.34°	+ 3.4°	
4	5.706	0.376	0.50	3.3	
4	7.600	0.500	0.60	3.0	
2	10.03	0.660	0.34	2.6	

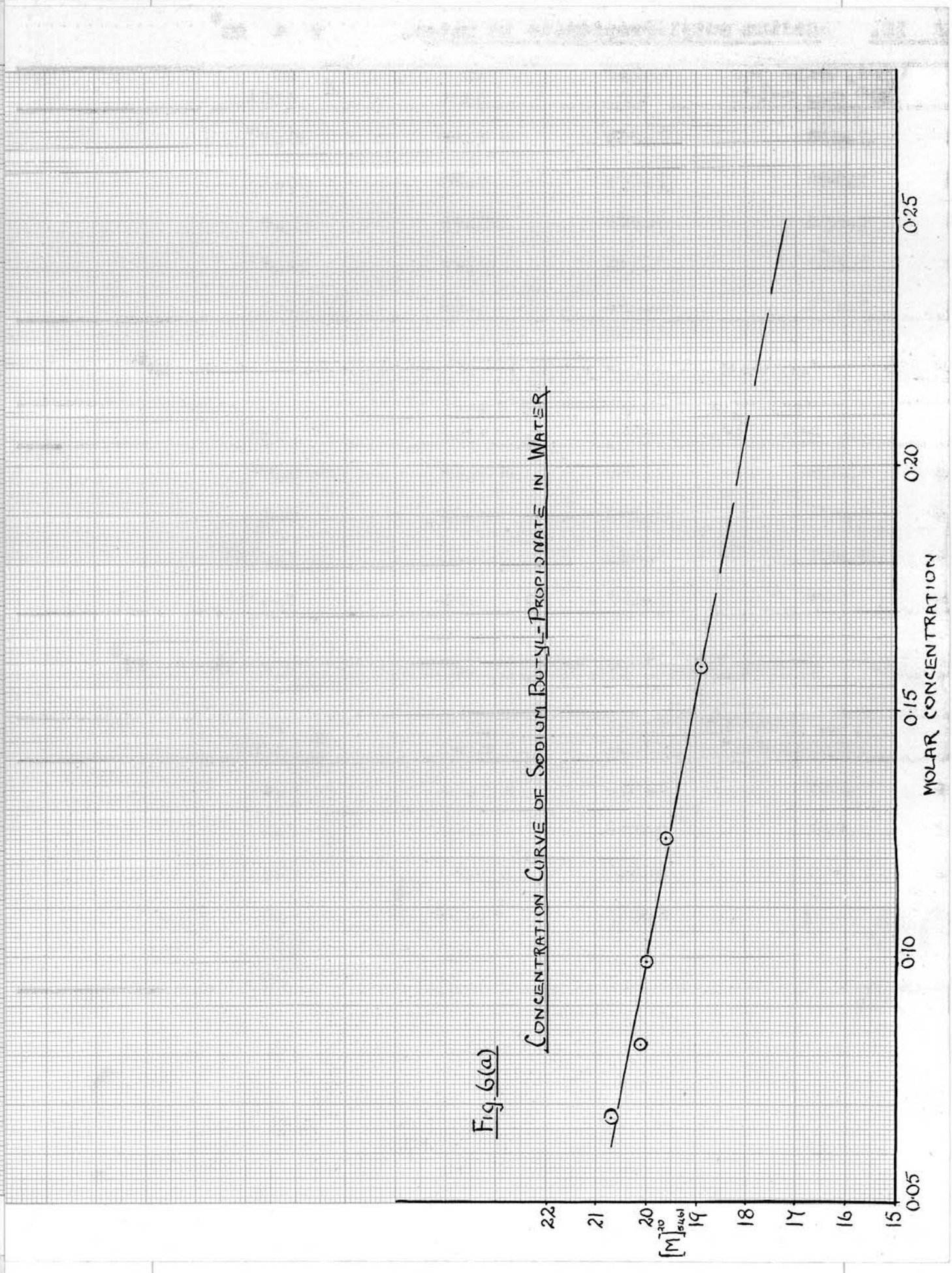

Concentration Curve of Sodium Butyl-Propionate in Water
$[M]^{20}_{equi}$
22
21
20
19
18
17
16
15
0·05
0·10
0·15
0·20
0·25
Molar concentration

Fig. 6(a)

dissociation. Bjerrum (1926) has shown that when two oppositely charged ions approach one another closer than a certain distance they become "associated" and behave like an undissociated molecule: it is possible that solvation of either or both of the ions will prevent the close contact and consequent association.

The rapid fall in rotation produced by adding water to alcoholic solutions of butyl-propionic acid can only be explained on the basis of increasing ionisation, since the effects of water association and refractive index are recognised as acting in the opposite direction. It was thus established (cf. Fig. 4) that

$$[M]\ \text{Acid}_{(alc)} > [M]\ \text{ion}_{(H_2O)}.$$

The concentration curves of sodium butyl-propionate in water, ethyl alcohol and propyl alcohol are shown in Figs. 6(a) and 6(b), details being given in Tables 12, 13 and 14. The sequence of values $[M]_{H_2O} > [M]_{C_2H_5OH} > [M]_{C_3H_7OH}$ might be explained by regarding the degree of ionisation in these solvents as the determining factor, and the fall in molecular rotation with increasing concentration as due to the decreased ionisation. In addition to this we would have the subsidiary association effects $H_2O > C_2H_5OH > C_3H_7OH$: so that the curves of Figs. 6(a) and 6(b) could be explained on the/

(TO FACE PAGE 83)

TABLE 16.

Sodium Butyl-Propionate in n-Propyl Alcohol - Water Mixtures. $T = 20^{\circ}$

l	grs. salt per 100 cc. sol^{n}.	Molar % H_2O in Solvent	α^{20}_{5461}	$[M]^{20}_{5461}$
4	3.801	0.0	$+ 0.34^{\circ}$	$+ 3.4^{\circ}$
4	3.799	34.9	0.19	1.9
4	3.798	61.1	0.34	3.4
2	3.804	90.2	0.43	8.6
		100.0		$\doteq$ 17.2 *
4	7.600	0.0	0.60	3.0
4	7.600	10.7	0.44	2.2
4	7.601	27.0	0.34	1.7
4	7.600	39.6	0.34	1.7
4	7.600	59.0	0.53	2.6(5)
4	7.600	82.4	1.01	5.0(5)
4	7.599	89.1	1.40	7.0
		0.0		$\doteq$ 2.0 **
4	15.20	21.6	0.31	0.7(8)
4	15.20	31.3	0.35	0.8(8)
4	15.20	53.9	0.49	1.2(3)
4	15.20	72.4	0.96	2.4
2	15.20	92.8	1.50	7.5

* cf. Fig. 6(a) ** cf. Fig. 6(b)

3.8 grs. salt/100 c.c. sol^{n}. = M/4 sol^{n}.

(TO FACE PAGE 83)

TABLE 15.

Sodium Butyl-Propionate in Ethyl Alcohol-Water Mixtures. T = 20°

ℓ	grs. salt per 100 cc. soln.	Molar % H_2O in Solvent	α^{20}_{5461}	$[M]^{20}_{5461}$
4	3.800	0.0	+ 0.86°	+ 8.6°
4	3.798	13.2	0.80	8.0
4	3.799	33.8	0.70	7.0
4	3.800	53.0	0.70	7.0
4	3.800	60.8	0.70	7.0
		100.0		≒ 17.2 *
4	7.599	0.0	1.49	7.4(5)
4	7.598	11.4	1.40	7.0
4	7.602	26.1	1.24	6.2
4	7.598	49.2	1.20	6.0
4	7.603	56.3	1.24	6.2

3.8 grs. salt/100 c.c. soln = M/4 soln. * cf. Fig. 6(a).

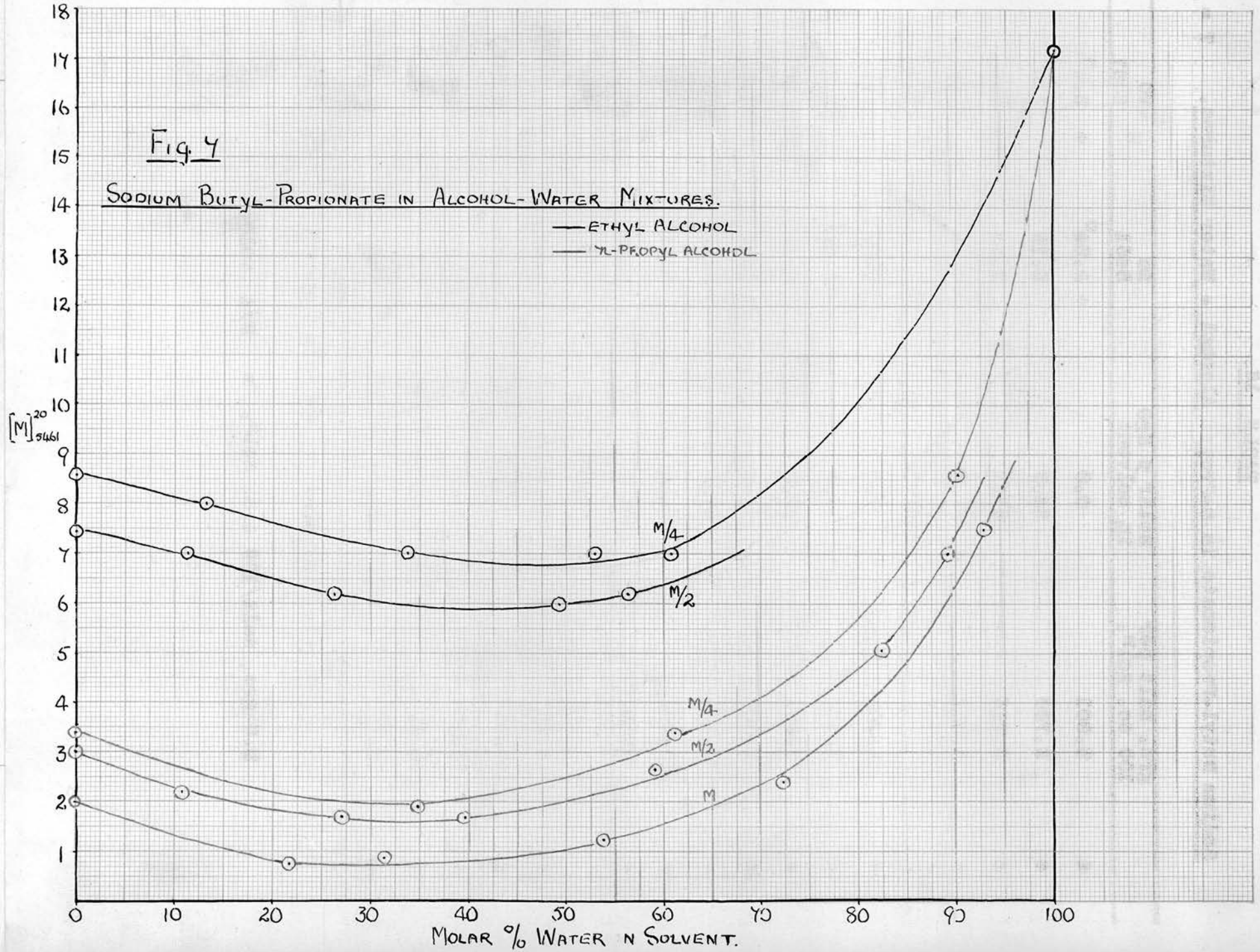


Fig 4
Sodium Butyl-Propionate in Alcohol-Water Mixtures.
Ethyl Alcohol
n-Propyl Alcohol
$[M]^{20}_{5461}$
M/4
M/2
M/4
M/2
M
0
10
20
30
40
50
60
70
80
90
100
Molar % Water in Solvent.

the basis

$$\text{ion}\,(H_2O) > \text{ion}_{(C_2H_5OH)} > \text{ion}_{(C_3H_7OH)} > \text{salt}$$

This simple view-point must be elaborated, when the alcohol-water curves for sodium butyl-propionate are examined (Fig. 7 and Tables 15 and 16). A minimum rotation exists which cannot be explained on an ionisation or association basis without assuming that either (a) propyl and ethyl alcohol - water mixtures have a minimum dielectric constant at a certain concentration in each case, or (b) the association of water and alcohol molecules with the sodium salt (or its ion) has a minimum at a certain water:alcohol ratio, the water and alcohol molecules associating together rather than with the salt or ion. It may be noted that the effect of this is to render the ratio salt: available solvent molecules large i.e. the solution appears to be more concentrated. This is then in agreement with the observations of Butler and co-workers (Proc. Roy. Soc., 1930, A 129, 519; 1931, A 131, 382) who showed that the addition of water to alcohol containing an alcoholated complex, does not result in the immediate replacement of alcohol by water. In this region we may suppose that the water molecules are more or less "bound" by the free alcohol molecules, and are not available for replacement purposes in the complex, until a definite water : alcohol ratio has been surpassed.

The/

The degree of ionisation of an acid such as butyl-propionic acid, when dissolved in water at a concentration $c = 5$ cannot be great. The effect on the rotation of adding water to alcoholic acid solutions is however large, and, as noted above, cannot easily be explained by a process other than ionisation: therefore the rotation of the ion to produce such a definite effect for a small ionisation must itself be very small or even negative. Thus we consider the series

$$\text{Acid} > \text{ion}_{(H_2O)} > \text{ion}_{(C_2H_5OH)} > \text{ion}_{(C_3H_7OH)} > \text{ion}$$

In considering the sequence of changes involved in the addition of water or an ionising solvent to the solid salt, we may take the first effect as the breaking up of the self association of the salt, followed by or simultaneously accompanied by the formation of the ions:

$$M(BP) + H_2O \longrightarrow M^{+}_{(H_2O)} + (BP)^{-}$$

The degree of ionisation of the salt will in the first place be determined largely by the extent of solvation of the cation: thus sodium and tetra-ethyl-ammonium ions may be reasonably expected to produce higher ionisation for a given salt : water ratio in this concentrated region than the less hydrated ions, potassium and ammonium. In this region, moreover, the anion will not in general be hydrated to a great extent:/

extent: this hydration will occur in a more dilute solution. One cannot, in general, determine the relative rotations of salt and unsolvated ion as represented by the above equation, but if the salt be considered as having roughly the same rotation as the unsolvated ion, since the ion is present in the salt before solution in an ionising solvent, then the only change in rotation on adding water in this initial stage will be due to the breaking up of the salt-salt complexes with presumably a fall in rotation in the case of salts of butyl-propionic acid. This will then be followed by a rise in rotation, due to the solvation of the anion.

In the case of sodium butyl-propionate, the addition of an ionising solvent may then be expected to give rotation curves of the form of Fig. 8.

Fig. 8.

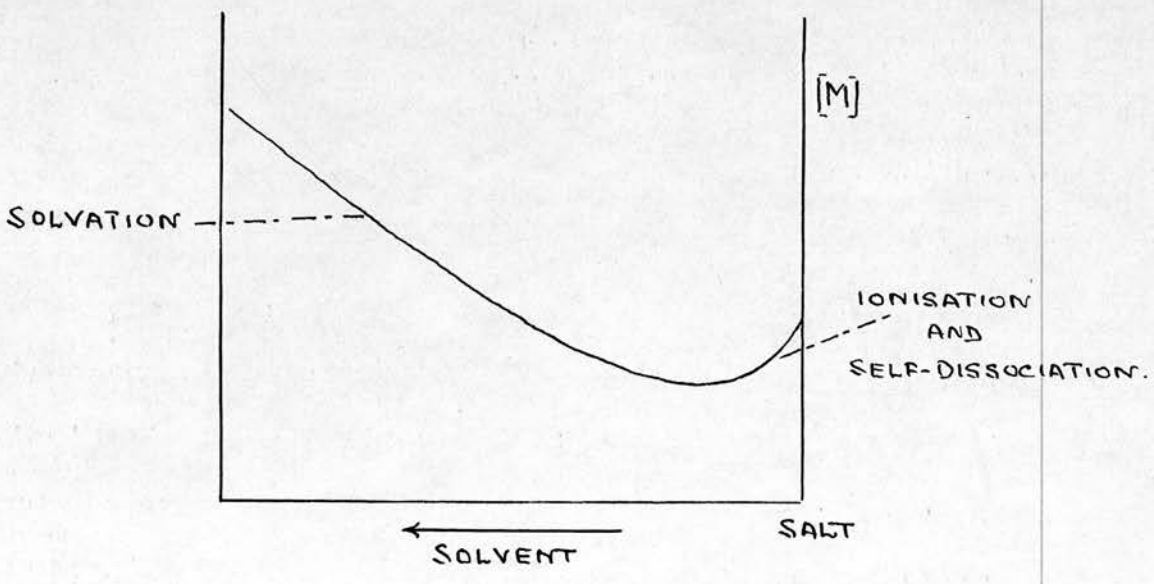
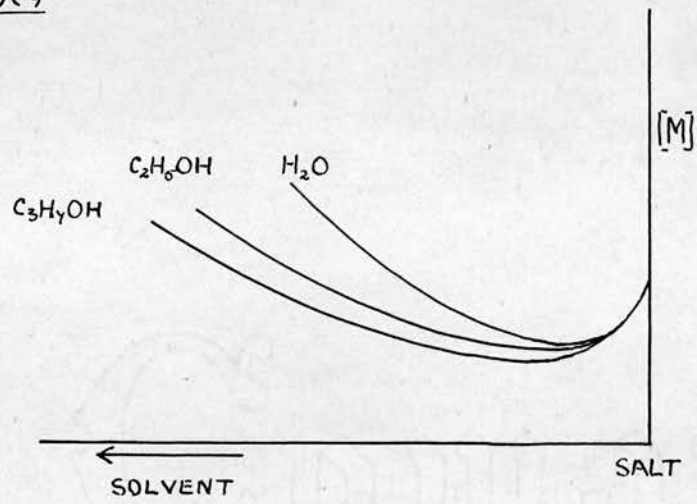


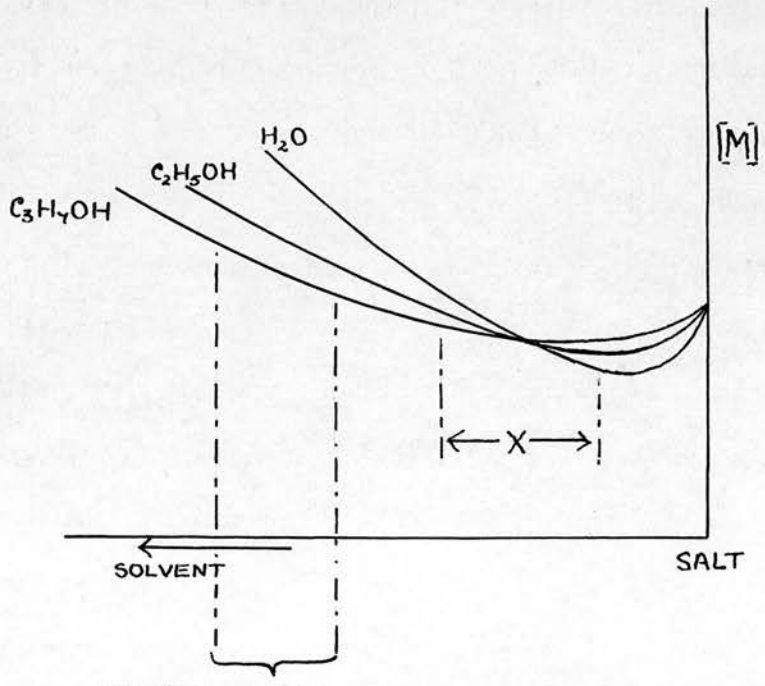
Fig. 9(a) shows the relative positions on the above basis of propyl alcohol, ethyl alcohol and water: experimental curves can only be obtained for the dilute region.

Fig. 9(a)



If the ion has a lower rotation than the salt, then the form of the curves in the concentrated region may be expected to be of the form shown in Fig. 9(b)

Fig. 9(b)



Now, to return to the alcohol-water curves for a given concentration of sodium butyl-propionate, the end points of the curves will of course correspond to the curves above for the given concentration where

$$[M]_{alc} < [M]_{H_2O}$$

At an intermediate ratio of water: alcohol, however, the concentration of salt with regard both to water and to alcohol appears to be very considerably increased by the presence of the other solvent, and the rotation will then be between the values for the concentrated solutions in the region indicated in Fig.9(b) (X) where both these rotations are well below those for the pure solvents at the initial concentration: the curve therefore shows a decided minimum at an intermediate water : alcohol ratio.

(TO FACE PAGE 88)

TABLE 17.

Tetra-Ethyl-Ammonium Tartrate in Water. T = 20°

l	grs. salt per 100 cc. soln.	Mols. solvent / mols. solute	α^{20}_{5461}	$[M]^{20}_{5461}$
1	30.48	54.8	+ 3.80°	+ 50.9°
1	20.28	92.1	2.70	54.3
2	10.20	202.9	2.85	57.0
2	5.144	421.1	1.47	58.3

TABLE 18.

Tetra-Ethyl-Ammonium Tartrate in Ethyl Alcohol. T = 20°

l	grs. salt per 100 cc. soln.	Mols. solvent / mols. solute	α^{20}_{5461}	$[M]^{20}_{5461}$
1	30.40	17.1	+ 5.60°	+ 75.2°
1	20.01	29.1	3.82	77.9
2	10.20	63.0	4.00	80.0
4	4.986	134.6	3.95	80.8
4	2.612	261.9	2.09	81.6

TABLE 19.

Tetra-Ethyl-Ammonium Tartrate in n-Propyl Alcohol. T = 20°

l	grs. salt per 100 cc. soln.	Mols. solvent / Mols. solute	α^{20}_{5461}	$[M]^{20}_{5461}$
1	7.225	70.9	+ 1.34°	+ 75.7°
2	4.948	106.3	1.77	73.0
4	3.790	139.4	2.62	70.5
4	2.628	203.3	1.70	66.0

(TO FACE PAGE 88)

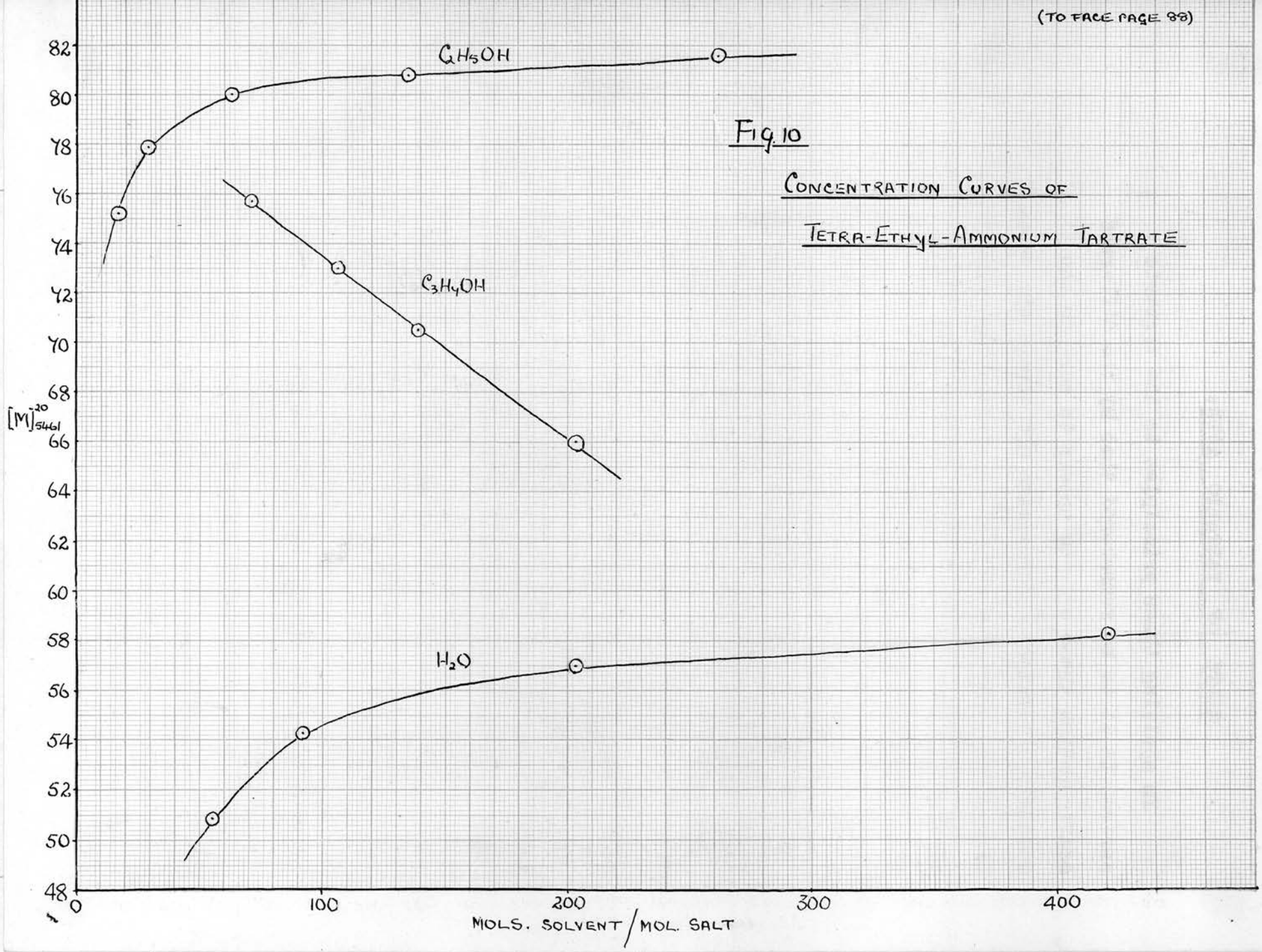


Fig. 10

CONCENTRATION CURVES OF

TETRA-ETHYL-AMMONIUM TARTRATE

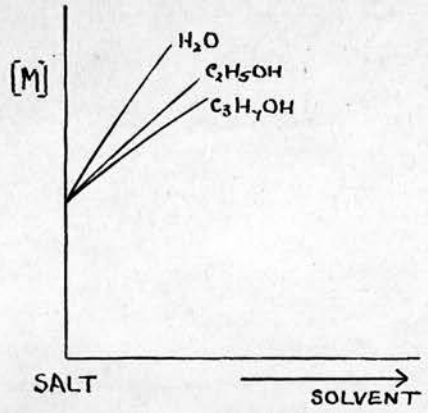
(b). SALTS OF TARTARIC ACID.

In applying these principles to the tartaric series, it is to be remembered that by the different configuration these effects appear to work in the opposite direction: association now lowers the rotation while ionisation of the acid raises the rotation, as already discussed (p.76). We therefore consider the reversed series (cf. p. 84)

$$\text{ION}_{(\text{SALT})} > \text{ION}_{(C_3H_7OH)} > \text{ION}_{(C_2H_5OH)} > \text{ION}_{(H_2O)} > \text{ACID}.$$

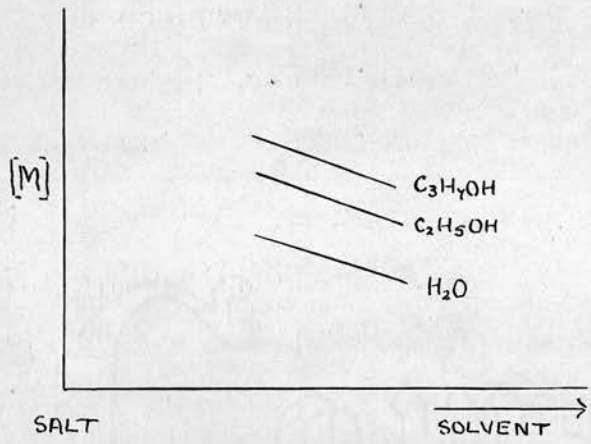
The concentration curves of tetra-ethyl-ammonium tartrate in water, ethyl alcohol and propyl alcohol are shown in Fig. 10, the molecular rotation being plotted against the ratio, mols. solvent/mols. solute. Tetra-ethyl-ammonium tartrate was chosen by reason of its greater solubility in the alcohols. The detailed results are given in Tables 17, 18, and 19.

Examining the system on the same principles as before we consider the addition of solvent as initially decreasing the self-association and increasing the production of the unsolvated ion. Both these effects are taken as producing a rise in rotation (Fig. 11).



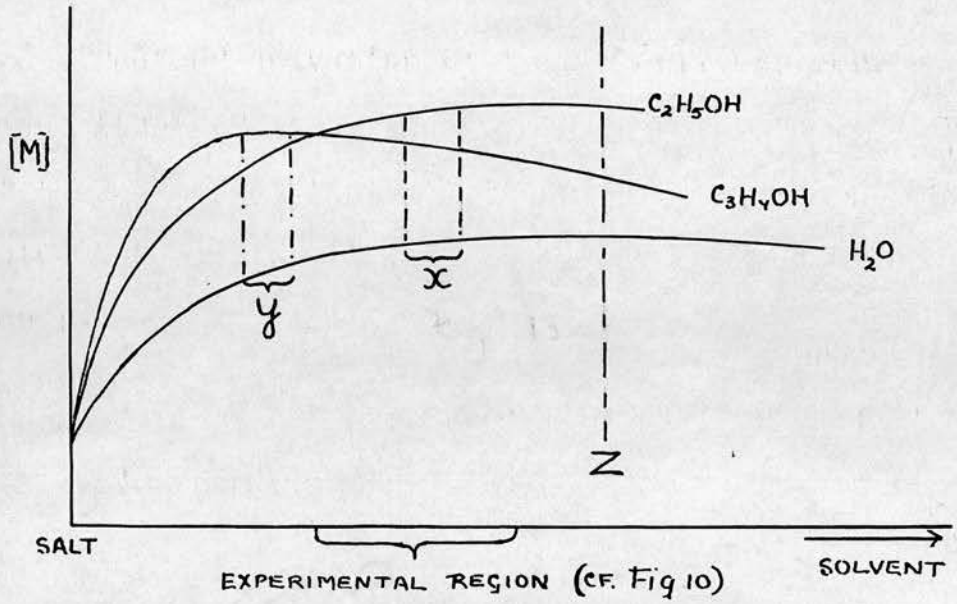
The effect of solvation of the anion, however, rapidly makes itself felt by reason of the nature of the anion: if the degree of ionisation were constant for a given solvent to salt ratio, we would have curves of the form:-

Fig 12



The greater ionisation effect of the water is thus partially counterbalanced by the rapidly growing effect of the water-anion association: a similar effect appears in the case of ethyl alcohol, but the curve as a whole is higher up in the rotation scale by reason of the less ethyl alcohol - ion association: while the ionisation in the case of propyl alcohol is relatively small, the predominant feature of the curve being the rapid rise due to the breaking up of the salt-salt complexes, (a process in which propyl alcohol has been shown to be specially efficient cf. p. 64), followed by the solvation of the salt or anion. The experimental curves may therefore be regarded as part of a complete scheme shown in Fig. 13.

Fig. 13



The alcohol - water curves for tetra-ethyl-ammonium tartrate, ammonium tartrate, and sodium tartrate are shown in Figs. 14(a), 14(b) and 14(c), the results being tabulated in the following Tables:-

TABLE 20.

Tetra-Ethyl-Ammonium Tartrate in Ethyl Alcohol-Water Mixtures.

T = 20°

ℓ	grs. salt per 100 cc. soln.	Molar % H_2O in Solvent	α^{20}_{5461}	$[M]^{20}_{5461}$
2	10.20	0.0	+ 4.00°	+ 80.0°
1	10.21	19.3	1.80	71.9
2	10.20	47.3	3.08	61.6
2	10.20	64.0	2.94	58.8
2	10.20	75.7	2.84	56.8
2	10.20	91.6	2.81	56.2
2	10.20	100.0	2.85	57.0

10.2 grs. salt/100 c.c. soln. = M/4 soln.

TABLE 21.

Tetra-Ethyl-Ammonium Tartrate in n-Propyl Alcohol-Water Mixtures.

T = 20°

ℓ	grs. salt per 100 cc. soln.	Molar % H_2O in Solvent	α^{20}_{5461}	$[M]^{20}_{5461}$
1	10.20	29.3	+ 1.51°	+ 60.4°
4	10.20	40.8	5.80	58.0
2	10.20	56.5	2.75	55.0
2	10.19	74.9	2.72	54.5
2	10.20	86.3	2.76	55.2
2	10.20	100.0	2.85	57.0

10.2 grs. salt/100 c.c. soln = M/4 soln.

TABLE 22.

Ammonium Tartrate in Ethyl Alcohol - Water Mixtures.

T = 20°

ℓ	grs. salt per 100 cc. soln.	Molar % H_2O in Solvent	α^{20}_{5461}	$[M]^{20}_{5461}$
4	4.601	80.7	+ 7.45°	+ 74.5°
4	4.601	84.8	7.34	73.4
4	4.599	90.4	7.25	72.5
4	4.602	96.6	7.21	72.0
4	4.601	100.0	7.20	72.0
4	9.201	89.1	14.74	73.6(9)
4	9.201	91.2	14.69	73.4(5)
4	9.202	94.1	14.67	73.3(3)
4	9.200	98.3	14.60	73.0(0)
4	9.200	100.0	14.62	73.1(0)

4.6 grs. salt/100 c.c. soln. = M/4 soln.

TABLE 23.

Ammonium Tartrate in n-Propyl Alcohol - Water Mixtures.

T = 20°

ℓ	grs. salt per 100 cc. soln.	Molar % H_2O in Solvent	α^{20}_{5461}	$[M]^{20}_{5461}$
4	4.599	84.6	+ 7.34°	+ 73.4°
4	4.599	86.2	7.29	72.9
4	4.602	90.3	7.24	72.4
4	4.601	92.0	7.20	72.0
4	4.599	95.2	7.15	71.5
4	4.602	96.4	7.16	71.6
4	4.600	98.2	7.18	71.8
4	4.601	100.0	7.20	72.0

TABLE 23 continued.

ℓ	grs salt per 100 cc. soln.	Molar % H_2O in Solvent.	α^{20}_{5461}	$[M]^{20}_{5461}$
4	9.201	91.8	14.75	73.7(4)
4	9.201	94.1	14.69	73.4(5)
4	9.202	95.5	14.67	73.3(3)
4	9.199	97.5	14.55	72.7(6)
4	9.202	98.4	14.55	72.7(3)
4	9.200	100.0	14.62	73.1(0)

4.6 grs. salt/100 c.c soln. = M/4 soln.

TABLE 24.

Sodium Tartrate in Ethyl Alcohol - Water Mixtures. T = 20°

ℓ	grs. salt per 100 cc. soln.	Molar % H_2O in Solvent.	α^{20}_{5461}	$[M]^{20}_{5461}$
4	4.850	86.8	+ 6.84°	+ 68.4°
4	4.851	88.6	6.88	68.8
4	4.849	93.0	6.92	69.2
4	4.850	96.3	6.95	69.5
4	4.850	98.3	6.99	69.9
4	4.851	100.0	7.01	70.1
4	9.698	90.7	13.53	67.6(6)
4	9.701	94.0	13.63	68.1(4)
4	9.702	95.6	13.69	68.4(2)
4	9.701	98.8	13.86	69.2(9)
4	9.701	100.0	13.93	69.6(5)
4	19.40	95.6	26.64	66.6(0)
4	19.40	98.2	26.99	67.4(8)
4	19.40	99.6	27.23	68.0(8)
4	19.40	100.0	27.26	68.1(5)

4.85 grs. salt/100 c.c. soln. = M/4 soln.

TABLE 25.

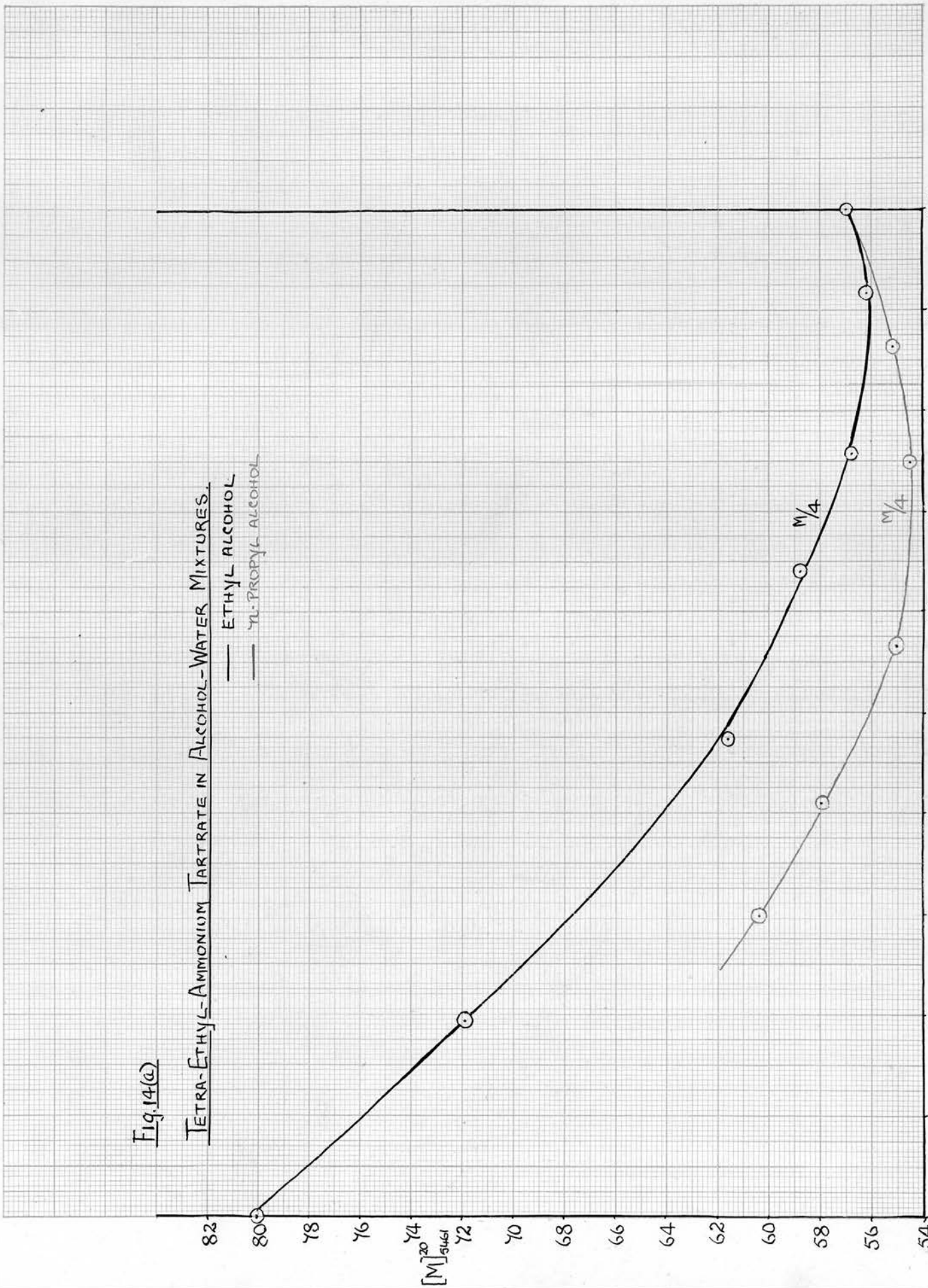
Sodium Tartrate in n-Propyl Alcohol - Water Mixtures.

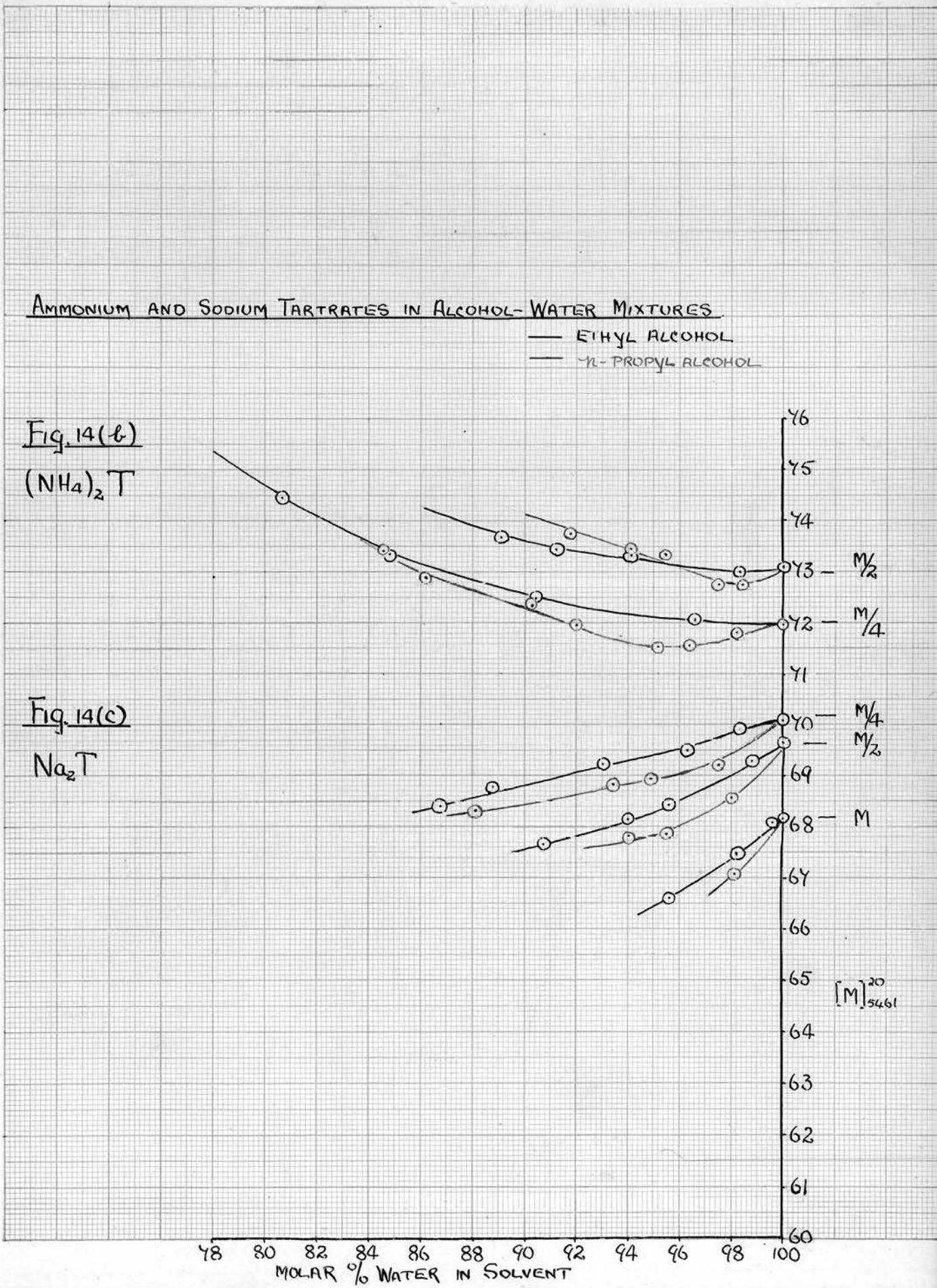
ℓ	grs. salt per 100 cc. soln.	Molar % H_2O in Solvent	α^{20}_{5461}	$[M]^{20}_{5461}$
4	4.850	88.1	+ 6.83°	+ 68.3°
4	4.849	93.4	6.88	68.8
4	4.849	94.9	6.89	68.9
4	4.850	97.5	6.92	69.2
4	4.851	100.0	7.01	70.1
4	9.700	94.0	13.56	67.8(0)
4	9.700	95.5	13.57	67.8(5)
4	9.702	98.0	13.72	68.5(7)
4	9.701	100.0	13.93	69.6(5)
4	19.40	98.1	26.83	67.0(8)
4	19.40	100.0	27.26	68.1(5)

4.85 grs. salt/100 c.c. soln. = M/4 soln.

Fig. 14(a)

Tetra-Ethyl-Ammonium Tartrate in Alcohol-Water Mixtures.




AMMONIUM AND SODIUM TARTRATES IN ALCOHOL-WATER MIXTURES
ETHYL ALCOHOL
n-PROPYL ALCOHOL
Fig. 14(b)
$(NH_4)_2T$
Fig. 14(c)
Na_2T
M/2
M/4
M/4
M/2
M
$[M]^{20}_{5461}$
76
75
74
73
72
71
70
69
68
67
66
65
64
63
62
61
60
48
80
82
84
86
88
90
92
94
96
98
100
MOLAR % WATER IN SOLVENT

The curves of sodium tartrate and tetra-ethyl-ammonium tartrate distinguish themselves from those of ammonium tartrate by reason of the fact that for the former the rotation falls with increasing concentration in water, while for the latter the rotation increases under similar circumstances, but in both types the addition of alcohol has a lowering tendency, shown more particularly in the case of propyl alcohol by the production of a minimum rotation: it is probable that the case of sodium tartrate is similar to that of tetra-ethyl-ammonium tartrate, though solubility limitations prevent the corresponding rotations from being obtained. The minimum for intermediate alcohol : water ratios is then determined by the fact that the effective concentrations of salt or ion with regard to the two solvents separately is such that the mean rotation is below that for the initial smaller concentration in water or in alcohol separately (cf. Fig. 13) as in the case of sodium butyl-propionate, discussed on p. 87 . If the solution be reasonably dilute then the ethyl alcohol - water value will lie above that of the propyl alcohol - water value (cf. Fig. 13 - region X): in a more concentrated solution, it is possible that the propyl alcohol - water curve will lie above that of the ethyl alcohol - water (cf. Fig. 13 - region Y). This is realised in the conditions/

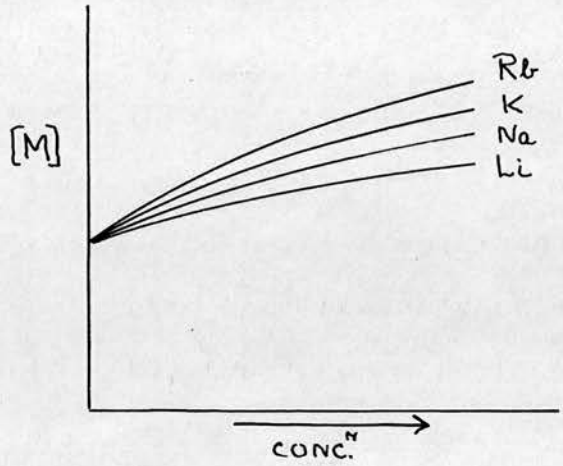
conditions for Fig. 14(b), for M/2 curves for ammonium tartrate.

In Fig. 13 the relative values for a solvent to solute ratio such as Z will be determined by the relative effects of ionisation and association in each solvent. Considering then one solvent alone, water, for different salts, the degrees of ionisation for a given molar concentration, will depend first on the degrees of hydration of the cation, and the consequent different degrees of approach of cation and anion. Now, from the series on which we have based the preceding considerations, the unsolvated anion, as present in a solid tartrate, corresponds to a greater rotation than the hydrated anion and hence we should expect that in aqueous solutions, an increasing degree of ionisation will, other things being equal, mean a decreasing rotation by reason of greater opportunities for hydration of the anion. Thus, regarding the degree of ionisation in these dilute solutions as being determined largely by the hydration of the cations, we would have

$$[M]_{Rb_2T} > [M]_{K_2T} > [M]_{Na_2T} > [M]_{Li_2T} .$$

If we consider any one of these tartrates, we would expect the rotation to decrease with dilution by reason of the greater opportunities for hydration of the anion : concentration curves, on this basis, would be of the form:-

Fig. 15.



where the very dilute solutions would have the lowest molecular rotation.

The experimental curves as obtained by Darmois show that the sodium and lithium tartrate curves are below the anion value. This may be regarded as due to the influence of the positive ions on the hydroxyl groups of the tartaric ion as a whole, as exemplified by the examples cited in the introduction (pp. 10-21): the final form of the concentration curves is thus taken as due to the two opposing influences of hydration and deformation of the anion. It may be noted that Darmois' explanation (Trans. Far. Soc. 1930, 26, 384) of these curves also involves these two factors, but both are regarded as acting in the opposite direction. His initial explanation given in 1928 (Ann. Phys. 1928, 10, 70) agrees with that advanced above.

ADDITION OF UREA AND GLYCEROL TO SODIUM AND AMMONIUM TARTRATES.

Any factor which decreases the apparent degree of dissociation of a tartrate or which tends to dehydrate the tartrate anion will therefore tend to cause a rising rotation. Thus the addition of salts, which are strong electrolytes to solutions of any one tartrate will cause a rise in rotation by reason of the general mass action equation

$$T^{--} + 2\,M^{+} \rightleftharpoons M_2T$$

though, in the case of addition of ions of the type of sodium and lithium, this effect will be more than counterbalanced by the deformation tendency. Thus curves similar to those given on p.16 (Introduction) were obtained by Darmois (Ann. Phys., 1928, 10, 70) and Long (Amer. Chem. Journal, 1888, 5, 351), for the addition of such electrolytes. The effect of addition of substances such as urea is capable of explanation on a similar basis. Urea is basic in character and in solution with tartrate ions will tend to form undissociated molecules of urea tartrate, with a consequent increase in rotation. At the same time one would not expect much deformation by the positive ion in this case; and hence the addition of urea to tartrates such as ammonium tartrate and sodium tartrate would produce a rise in rotation. Tables 26 and 27 and Fig.16 show the experimental results: a rapid rise follows the addition of urea in both cases.

TABLE 26.

Addition of Urea to Aqueous Sodium Tartrate Solutions (M/4)

$T = 20^{\circ}$

ℓ	grs. tartrate per 100 cc. soln.	Molar Conc. of Urea.	α^{20}_{5461}	$[M]^{20}_{5461}$
4	4.851	0.00	$+ 7.01^{\circ}$	$+ 70.1^{\circ}$
4	4.850	0.50	7.15	71.5
4	4.851	1.00	7.34	73.4
4	4.850	2.21	7.75	77.5
4	4.851	3.00	7.95	79.5

TABLE 27.

Addition of Urea to Aqueous Ammonium Tartrate Solutions (M/4)

$T = 20^{\circ}$

ℓ	grs. tartrate per 100 cc. soln.	Molar Conc. of Urea.	α^{20}_{5461}	$[M]^{20}_{5461}$
4	4.601	0.00	$+ 7.20^{\circ}$	$+ 72.0^{\circ}$
4	4.599	0.50	7.40	74.0
4	4.601	1.09	7.60	76.0
4	4.600	2.01	7.96	79.6
4	4.600	3.01	8.20	82.0

TABLE 28.

Addition of Glycerol to Aqueous Sodium Tartrate Solutions (M/4)

$T = 20^{\circ}$

ℓ	grs. tartrate per 100 cc. soln.	Molar Conc. of Glycerol	α^{20}_{5461}	$[M]^{20}_{5461}$
4	4.851	0.00	$+ 7.01^{\circ}$	$+ 70.1^{\circ}$
4	4.850	0.26	7.00	70.0
4	4.850	0.53	7.04	70.4
4	4.852	1.06	7.07	70.7
4	4.851	2.30	7.22	72.2
4	4.851	3.13	7.24	72.4
4	4.851	3.99	7.32	73.2

TABLE 29.

Addition of Glycerol to Aqueous Ammonium Tartrate Solutions (M/4)

$T = 20^{\circ}$

ℓ	grs. tartrate per 100 cc. soln.	Molar Conc. of Glycerol	α^{20}_{5461}	$[M]^{20}_{5461}$
4	4.601	0.00	$+ 7.20^{\circ}$	$+ 72.0^{\circ}$
4	4.599	0.52	7.21	72.1
4	4.600	1.04	7.26	72.6
4	4.601	2.04	7.40	74.0
4	4.599	3.01	7.47	74.7

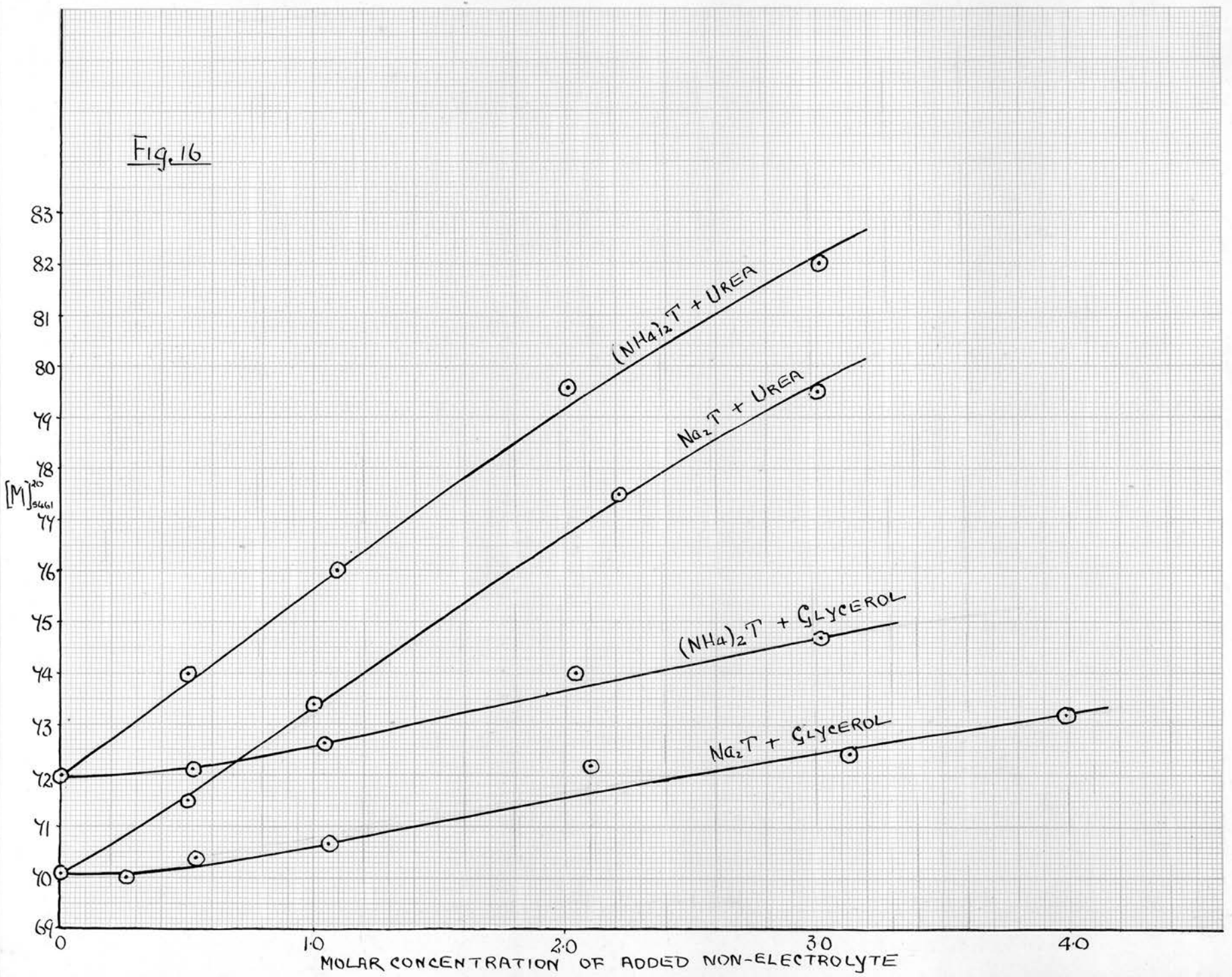


Fig. 16
83
82
81
80
79
78
77
76
75
74
73
72
71
70
69
$[M]^{20}_{5461}$
0
1·0
2·0
3·0
4·0
MOLAR CONCENTRATION OF ADDED NON-ELECTROLYTE
$(NH_4)_2T$ + UREA
Na_2T + UREA
$(NH_4)_2T$ + GLYCEROL
Na_2T + GLYCEROL

Fig. 16 (Tables 28 and 29) also shows the effect of adding glycerol to similar solutions. By reason of the number of hydroxyl groups in the glycerol molecule, the effect of such addition will be the disturbance of the water - anion equilibrium in the sense of dehydration of the anion with a consequent rise in rotation, if the solution be originally fairly dilute with respect to the tartrate. At the same time, for a more concentrated solution of tartrate a minimum might be expected for the same reasons as the minimum with propyl alcohol-water mixtures: there is slight evidence for this in both cases.

It will thus be observed that an attempt has been made in the preceding pages to explain the variations in optical rotatory power of tartaric acid and tartrates without introducing the conception of two molecular forms for the tartrate complex. In recent years evidence has been put forward (Bruhat, Trans., Far. Soc. 1930, 26, 400) in support of the view that the existence of separate molecular forms is not a necessary consequence of the existence of two centres to which corresponding rotatory dispersions may be related. In view of the fact that the rotatory dispersions are undoubtedly connected with two regions of absorption, it is not improbable that these are determined by the presence of two absorbing groups in the one tartaric acid molecule. These groups would then be presumably the -OH and -COOH groups, with the expectation that the latter would be particularly susceptible to external conditions. The remarkable variations in optical rotation and dispersion for various environments are then to be reasonably attributed to the varying electron arrangements in these groups, with corresponding alterations in the absorption spectrum.

SUMMARY AND CONCLUSIONS.

The rotations of d- α -n-butyl-propionic acid and its methyl ester have been examined in various organic solvents, and correlated with the refractive indices of the media, in the sense that a relatively high refractive index corresponds to a relatively low rotation. This relationship is subject to constitutional influences: for example rotations of the ester in solvents of the benzene type are higher than the values expected from refractive index considerations as applied to the methane type of solvent, but in each group separately, the inverse relationship between refractive index and rotatory power is in general respected. In certain instances the dipole moment of the solvent exerts a modifying influence, a high dipole moment tending to raise the rotation. Examination of these and other factors has led to the conclusion that the dextrorotatory acid and ester possess an L - configuration.

In aqueous and aqueous-alcoholic solutions of d- α -n-butyl-propionic acid and its sodium salt, it is considered that the effect due to variation in refractive index is small in relation to the changes produced by ionisation, association and solvation. Association and solvation are taken as raising the rotation, while ionisation lowers it.

The/

The rotations of tartaric acid and its sodium, ammonium and tetra-ethyl-ammonium salts have also been examined in aqueous and aqueous-alcoholic solutions, and discussed on similar principles. Contrary to d- butyl-propionic acid, the dextrorotatory tartaric acid is associated with a D- configuration: ionisation now raises the rotation while association and solvation lower it. For the given conditions the effect of the variation in the refractive indices of the media is regarded as negligibly small. The data given for aqueous solutions of salts of tartaric acid have been discussed on the assumption that two main influences act in opposition, one bearing on the relative rotations of undissociated salt and solvated anion, and the other exemplified by the known effects of positive ions on non-ionisable molecules containing hydroxyl groups.

The writer desires to acknowledge her indebtedness to Dr H.G. Rule and Dr N. Campbell, for the helpful advice and criticism, given during the course of this investigation.
